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Properties of Apparel Wools

II. Modification of Fiber Surface During Worsted Processing*

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Contribution from Textile Research Institute, Princeton, New Jersey

Abstract

Modification of the fiber surface during processing has been studied on three wools of Australian fine, domestic fine, and domestic medium grades. Samples were taken from each wool at each stage of their manufacture into a worsted fabric by the Forstmann Woolen Company. Groups of fibers, selected randomly from each sample, were treated with Pauly reagent and examined microscopically. The amount of color on the fiber was estimated visually, and the amount of scale disturbance was assessed. The rate of exhaustion of Anthraquinone Blue SKY was also measured on samples from each processing stage.

A consistently increasing amount of surface modification was observed with all three wools as the manufacturing process advanced. The susceptibility of the wools to staining with Pauly reagent and their rate of taking up Blue SKY from a dye bath also increased. However, all of these changes were reversed by a steaming process such as is frequently used in normal worsted processing. It was concluded that the dye susceptibility of processed wool is related to the amount of scale disturbance of the fibers and that the epicuticle does not seem to constitute the only major resistance to dye penetration.

Introduction

A summary of the internationally sponsored Wool Research Project of Textile Research Institute was given in Part I of this series. As part of this project, four large lots of wool were manufactured into fabric under carefully controlled conditions by the Forstmann Woolen Company. The Institute made extensive physical and chemical measurements on single fibers and on fiber assemblies from these wools at each stage of the manufacturing process. One aspect of these studies was an examination of the modification of the surface structure of fibers as they move through various mill operations. The results of this examination are reported in this paper, and details of other phases of the wool project will be presented in succeeding papers in this series.

The surface properties of wool fibers may be studied by several methods, including partial dyeing.

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differential staining, and the evaluation of surface friction. The Pauly test was selected as the primary method for differentiating the stages of processing in the various wool lots. It was supplemented by direct microscopic observation of scale condition and by measurement of dye-bath exhaustion rates. With each technique, data were taken in such a way that a statistical evaluation could be made.

Experimental

Materials

Three of the four Wool Research Project master wools were used for this study of surface modification: an Australian merino wool of 70's grade, an American Rambouillet wool of 64's grade, and an American crossbred wool of 58's/60's grade, the last being a mixture of Columbia, Targhee, and Corriedale types. These wools were processed on the worsted system by the Forstmann Woolen Company, and samples from the following process steps were available for this study: scoured wool, top, roving, yarn, steamed yarn, grey fabric, and ready-to-dye fabric. A few samples of top and roving which had been steamed at the Forstmann Woolen Company were also available. The steaming equipment and processing cycles used on the roving and yarns were identical, but the top process differed in both equipment and cycle; maximum wet- and dry-bulb temperatures corresponded for all three types of materials. For top, the steaming cycle consisted of 5 min. for reaching the processing temperature, 5 min. at temperature, and 5 min. cooling. The cycle was repeated three times. For roving and yarn, the time allowed for each stage was 10 min. and only one cycle was used. In each case, the processing temperature was approximately 185°F dry bulb and 175°F wet bulb.

Clean samples were prepared in the laboratory from each grease wool by washing with ether, alcohol, and water.

Pauly Test and Microscopic Examination

For each sample to which the Pauly test was applied, 100 fibers were randomly selected and fastened at the ends with Permount to microscope slides. Ten fibers were mounted on each slide. Five slides were placed in one reagent bath and five in another.

The Pauly reagent was prepared according to the method of Burgess and Rimington [2] by diazotizing sodium sulfanilate, filtering off the diazobenzene sulfonic acid, and dissolving it in sodium carbonate solution. Two baths of the reagent were required to handle all the fibers tested; they were prepared separately from the same stock solution. The slides holding the mounted fibers were immersed in the reagent bath for 10 min. and then washed with several portions of distilled water.

The stained fibers were then examined under a microscope. Each fiber was observed at three locations, which were selected in such a way that operator bias was eliminated, and two estimates of fiber condition were made at each position. First, the quarter-fractions of the fiber which had been colored by the reagent were recorded as one of the following figures: 0, 1, 2, 3, 4. No color was represented by 0, and complete coloration by 4. Second, the scale condition was estimated, using the following notation: *a*, scales normal; *b*, distal ends of scales raised; *c*, some scales removed or destroyed; *d*, no scales evident. These various scale conditions are represented diagrammatically in the inset in Figure 2. Such estimates depend on a subjective judgment of the operator but are reproducible. The fibers and the selected fields of view are identified so that the results can be checked by subsequent re-examination.

Dye Exhaustion Rates

The difficulty of following rapid changes in dye-bath concentrations by removing small samples, which were subsequently returned, led several workers [4, 8, 10] to devise methods for circulating a dye bath through a colorimeter or spectrophotometer so that changes could be measured quickly and, if necessary, continuously. For the exhaustion tests reported here, the temperature was chosen so that the rate of dyeing would be slow enough to permit the intermittent sampling technique. With the dye and temperature used, this rate of dyeing was so slow that stirring was found to be not necessary [8].

Samples containing 1.0 g. of dry domestic medium wool were dyed in a 70:1 dye bath containing 2% Anthraquinone Blue SKY, 10% sodium sulfate, and 3% sulfuric acid (based on sample weight). Each dye bath was prepared from stock solutions of the salt, the acid, and the dye, which is a monocomponent, level-dyeing type. The temperature was held at 45°C throughout the dyeing, and the pH was observed to change from 2.8 to about 3.2. The wool samples were cut into ½-in. lengths to facilitate their dispersion in the bath. It was found that chopping

TABLE I. PAULY TEST—DATA ON DYEING

A—Processing Effect

Wool type	Bath No.	Wool (lab. cleaned)	Scoured wool	Top	Roving	Yarn (steamed)	Grey cloth	Ready-to-dye cloth
		Sums for 50 fibers of fractions stained, coded by multiplying by 4						
Australian fine	1	17	96	251	327	98	124	350
	2	30	263	290	333	79	152	379
Domestic fine	1	65	159	238	345	120	149	344
	2	61	180	250	352	93	208	396
Domestic medium	1	62	137	288	351	47	194	355
	2	50	169	302	391	83	259	485

B—Steaming Effect

	Bath No.	Domestic medium top	Domestic medium roving	Domestic medium yarn	Domestic fine yarn
		Sums for 50 fibers of fractions stained, coded by multiplying by 4			
Steamed	1	246	104	47	98
	2	203	121	83	79
Unsteamed	1	288	351	381	345
	2	302	391	468	370

the fibers as short as ¼ in. does not affect the dyeing rate under the conditions used in this experiment; however, it should be noted that this is not always the case [8].

The exhaustion of the dye bath was measured colorimetrically on 2-ml. samples at predetermined times with a Fisher Electrophotometer. After the transmission measurement was made, the sample was returned to the dye bath. For each lot of wool investigated, two separate samples were tested on different days. The exhaustion of the dye bath was calculated from the transmission data by using a standard curve made with dye solutions of known concentration. By using short-light-path cells, so that the original dye bath had a transmission of 45% or more, a straight line was obtained for plots of log transmittance against concentration.

Results

Comparison of the amount of Pauly reagent absorbed by the fibers is shown quantitatively in Figure 1 and Table I. In the figure, no differentiation is made between the reagent baths, so that the maximum value of the index (the ordinate) would have been 1200 if all fibers had been dyed completely.

The scale condition of the various samples is represented by the data in Table II and Figure 2. Data

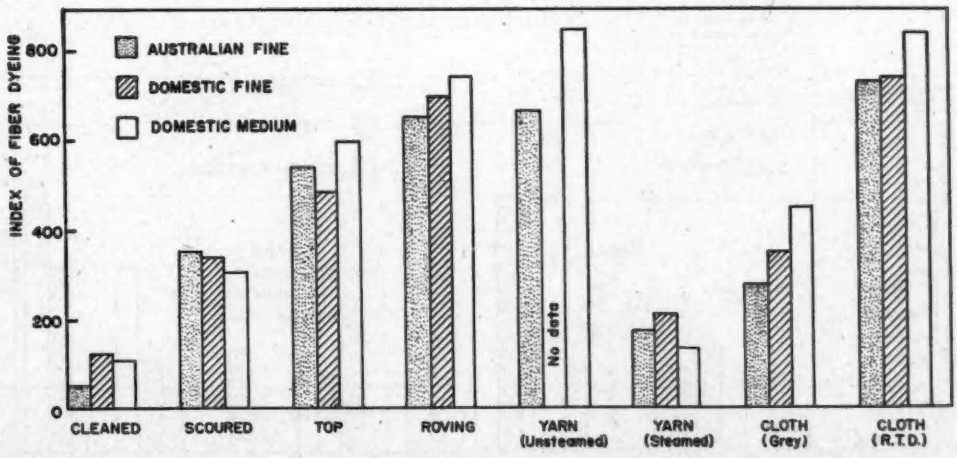

FIG. 1. *Comparison of the amount of Pauly reagent absorbed by wool fibers at different stages of processing.*

TABLE II. PAULY TEST—DATA ON SCALE CONDITION

Wool type	Bath No.	Percent (× 1.5) of microscope fields which show scales raised or removed: Wool (lab. cleaned)	Scoured wool	Top	Roving	Yarn (steamed)	Grey cloth	Ready-to-dye cloth
Australian fine	1	0	4	8	14	2	8	6
	2	2	6	16	15	1	6	29
Domestic fine	1	1	1	9	21	17	6	11
	2	3	17	10	39	6	17	32
Domestic medium	1	2	5	7	24	0	17	22
	2	4	13	13	31	2	25	38

from both reagent baths were consolidated in preparing Figure 2.

Figures 3 and 4 and Table III represent the data obtained in dye-bath exhaustion tests. Figure 3 compares unsteamed samples with their steamed counterparts, while Figure 4 shows progressive effects of processing, with steaming steps omitted. (This statement is not intended to imply that steaming of yarns is not standard practice for the fabrics produced in the Wool Research Project.) The results shown in Figure 3 confirm the change in dye exhaustion rate due to processing which was observed by Royer [6].

All three sets of data have been analyzed statistically, and the following discussion is based on these analyses. The details of the statistical analysis are found in the Appendix.

Discussion of Results

Two distinct effects are obvious from any one, or all, of the sets of data. First, progressive processing results in external surface modification, greater dye susceptibility, and a greater number of fibers whose scales are visibly raised at the distal end. Second, steaming reverses these effects. These results suggest that certain concepts concerning the epicuticle, as proposed by Lindberg, Mercer, Philip, and Gralén [3, 5], should be modified, especially with regard to the role of this membrane in the dyeing process. Lindberg and his coworkers have concluded that the epicuticle is a continuous sheath of chemically resistant material which covers the whole fiber, and that ruptures in this sheath provide the chief means for the dye molecules to enter the fiber.

The present data indicate that the scale condition may be important as a controlling element in dyeing. The decreased dye susceptibility caused by steaming could hardly be attributed to repair of ruptures in a resistant epicuticle. However, it is associated with the return of the scales to a flattened position, as can be confirmed visually. Instead of covering the scales externally as a continuous sheath, the epicuticle may actually surround each scale individually and leave some uncovered areas beneath the scales

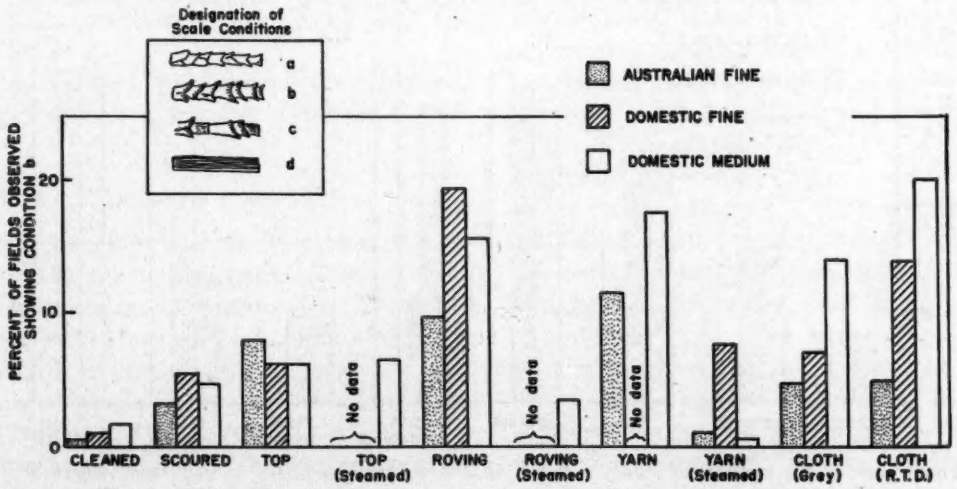

FIG. 2. *Comparison of the scale condition of wool fibers at different stages of processing.*

TABLE III. DYE-BATH EXHAUSTION MEASUREMENTS

Time (min.)	Exhaustion of bath (%) Wool (lab. cleaned)	Scoured wool	Top	Roving	Roving (steamed)	Yarn	Yarn (steamed)	Ready-to-dye cloth
15	18.5	34.0	31.0	34.0	22.5	30.5	18.5	42.0
	16.5	28.5	26.5	31.0	23.5	30.0	18.5	36.0
30	24.0	46.5	50.0	51.5	38.5	47.0	31.5	58.5
	26.5	44.0	44.0	49.0	40.0	46.0	33.5	56.0
45	28.5	57.5	61.0	64.0	47.0	58.5	36.0	76.5
	31.0	56.0	58.5	65.0	53.5	61.5	43.5	71.0
60	34.0	66.0	71.5	74.0	61.0	71.0	48.5	82.5
	35.5	66.5	69.5	73.5	61.5	73.5	48.5	81.0
80	39.5	76.5	84.0	86.5	71.5	81.0	56.5	91.0
	45.0	76.0	80.0	83.5	71.5	81.0	58.5	87.5
100	45.0	82.5	91.5	92.5	76.0	91.5	61.5	93.5
	48.5	86.0	89.0	91.0	81.5	88.5	66.5	91.5
130	49.0	88.0	96.0	94.0	86.0	93.5	73.5	96.0
	58.5	91.0	92.5	91.5	89.0	91.5	78.5	93.0
160	58.5	91.0	96.0	96.0	91.0	96.5	81.0	96.0
	61.0	93.5	93.5	93.5	92.0	93.5	83.0	93.0
190	66.0	91.5	97.0	97.5	91.5	96.5	86.5	96.0
	68.5	93.5	93.5	94.0	93.5	93.5	89.0	93.0
220	71.0	93.5	98.5	98.5	93.0	97.0	89.5	96.5
	76.0	94.0	94.0	96.0	94.0	94.0	91.5	94.0

through which dyes could easily penetrate when the scale is lifted.

The Pauly test yields results that are more sensitive to change than those from dye-bath exhaustion rates, as evidenced by the samples of top, roving, and yarn. These three are clearly differentiated by the Pauly test, but in the rate studies, top and yarn are not apparently different, and the dye exhaustion rate for roving is somewhat higher than for either of the others. It may therefore be concluded that dye-bath exhaustion, which is the easier and quicker technique, will differentiate large changes, but is less likely to pick up the smaller ones. A less level dye might improve the sensitivity of this method.

A distinct difference in the activity of the two baths of Pauly reagent was very apparent. It may be attributed to lack of equivalence in the preparation or stability of the two reagent baths. Methods of producing controlled reagent solutions are being studied.

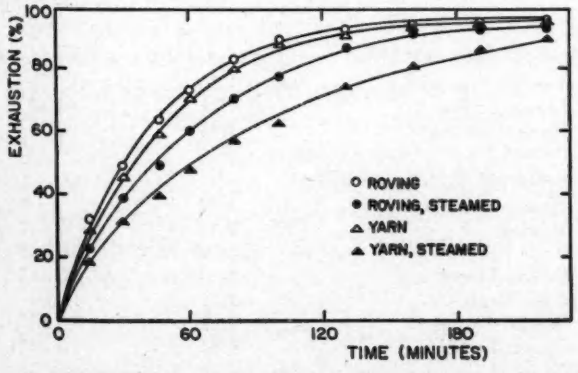

FIG. 3. *Effect of steaming on the rate at which domestic medium wool roving and yarn exhaust Anthraquinone Blue SKY from an acid bath at 45°C.*

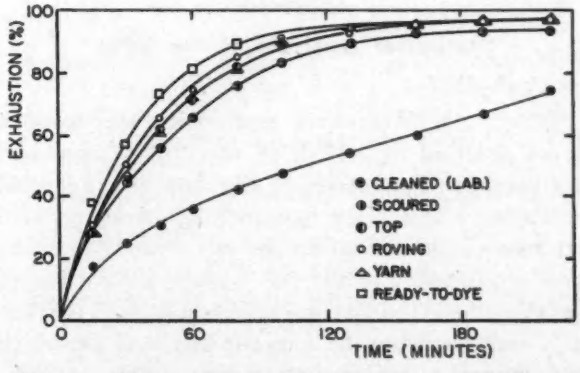

FIG. 4. *Effect of processing on the rate at which a domestic medium wool exhausts Anthraquinone Blue SKY from an acid bath at 45°C.*

The failure to detect a pure effect of wool type may be due to a truly common reaction to processing of all wool of nearly equal grade, or it may merely represent insufficient precision to detect these effects. Even if real and detectable, such effects would apparently be small in comparison to treatment effects. The existence of a wool-treatment interaction is evidence of unequal responses of different wools either to the treatments or to the dye.

Conclusions

1. The processing of wool effects surface modifications which are visible under the optical microscope.
2. Steaming of processed wools reverses the surface modification to such a degree that the steamed samples nearly approach the condition of unprocessed wool.
3. The surface modifications effected by processing may be evaluated by partial dyeing or by dye-bath exhaustion methods.
4. The dye susceptibility of processed wools is related to the amount of scale disturbance of the fibers, and the epicuticle does not appear to be the only major factor in resisting dye penetration.

Future Work

The results presented here suggest a considerable amount of further work. Investigations of aging characteristics, efficiency of steaming processes, variables in the steaming process, fiber stress during the steaming process, relaxation media other than steam, felting actions, and tippy dyeing characteristics are among the subjects on which information is lacking. Improvement of the reproducibility of the Pauly dye baths and improvement of the precision of the dye-bath exhaustion tests are also to be desired.

Appendix

Statistical Analysis of the Data

1—Pauly Test

Since 2,700 fibers were studied in these tests, it is not practical to publish all the original data and calculations. Summaries of the data are presented in Tables I and II, and summaries of analyses of variance [1, 7] are shown below. All 2,700 fibers were not included in any one analysis since a few of the steaming classifications were incomplete, particularly with respect to the domestic fine wool lot, which was the first to undergo processing.

a—Mechanical Processing.—The following table summarizes the analyses of the data given in Part *A* of Table I designed to show the effects of wool lot, *W*, processing treatment, *T*, and Pauly dye bath, *B*.

Source of variance	Sum of squares	Degrees of freedom	Mean square
Wool (*W*)	35.43	2	17.71
Treatment (*T*)	3916.74	6	652.79†
Bath (*B*)	75.35	1	75.35*
WB	8.99	2	4.50
WT	98.61	12	8.22*
BT	61.65	6	10.27*
WBT	69.44	12	5.79
Between fibers	7725.35	2058	3.75*
Within fibers	6373.03	4200	1.52

* In this and subsequent tables the asterisk (*) and double asterisk (**) are used as designations of statistical significance at the 5% and 1% levels, respectively.

† Cannot be tested directly because of the existence of both *WT* and *BT* interactions.

It is not surprising that the variance between fibers is significantly greater than that within fibers (*i.e.*, between fields on the same fiber). For future work, single readings on each fiber would therefore appear to be adequate.

The bath effect is apparent both in the interaction with treatment and as a main effect. The interaction is due to samples from the same processing treatment reacting differently in the two baths. That the two baths are different is undoubtedly due to lack of sufficient control in the preparation of the dye baths.

The wool-treatment interaction indicates that the different wools react differently to the processing treatments. With this situation existent, the establishment of pure wool and treatment effects is unimportant. However, existence of a treatment effect appears probable.

Summaries of the main effects are presented below with least significant differences (L.S.D.) [9]; the usual designation (*) indicates significance at the 5% level.

Tables of this type provide a means of investigating

Wools (L.S.D. = 0.13)	Average/field	Differences
Domestic medium	1.51	
Domestic fine	1.41	0.10
Australian fine	1.33	0.08
Treatments (L.S.D. = 0.19)		
Ready-to-dye cloth	2.57	
Roving	2.33	0.24*
Top	1.79	0.54*
Scoured wool	1.23	0.56*
Grey cloth	1.21	0.02
Steamed yarn	0.58	0.63*
Cleaned wool	0.32	0.26*
Baths (L.S.D. = 0.11)		
#1	1.57	
#2	1.35	0.22*

the location of significant effects when more than two items (*e.g.*, treatments) are being compared. Interaction may be investigated in the same manner.

Since some nonadditivity can be detected in the data, analysis of the logarithms of the original data was investigated. The conclusions were not affected.

b—Steaming.—The following analysis of variance of the data given in Part *B* of Table I shows a study of the steaming effect, *S*, based primarily on samples of the domestic medium wool lot, for which the greatest amount of steaming information is available:

Source of variance	Sum of squares	Degrees of freedom	Mean square
S	1528.01	1	1528.01*
BS	50.33	7	7.19
TS	294.61	3	98.20*
Between fibers	2993.32	787	3.80*
Within fibers	2495.01	1600	1.56

Both main steaming effects and steaming-treatment interactions are significant. The interaction is due to the different steaming process employed on the top in comparison to that on roving and yarn, and to the different forms (balls, spools, etc.) charged to the steamers. Although the bath-steaming interaction is not significant, it is suspiciously large ($P = 6\%$).

c—Scale Condition.—The data for this study are shown in Table II. The summary of the analysis of variance follows:

Source of variance	Sum of squares	Degrees of freedom	Mean square
Wool (*W*)	306.9	2	153.5
Treatment (*T*)	2646.1	6	441.0**
Bath (*B*)	466.6	1	466.6*
Residue (error)	2773.3	32	86.7

Interactions are all insignificant with respect to error, and are pooled into the last term in this table. As in the Pauly test, no main wool effect is found. Both bath and processing treatment effects are again evident, but the loss of interactions indicates that this method of assessing fiber modification will not yield as extensive information as may be obtained from the Pauly test. Thus, measurement of scale condition should be expected to produce data that are capable of theoretical interpretation regarding the character and function of the epicuticle, but should not be used when process differentiation is of primary importance.

2—Dye-Bath Exhaustion in Bulk Dyeing

The data for these studies are reported in Table III. Replicate runs were made, the top figure at each time period being from the first run and the lower being from the second run. Complete duplication of time intervals in all runs allows analysis of variance, with effects of treatments, *T*, time, θ, and treatment-time interaction, $T\theta$, being estimated. A summary of the results of this analysis provides the following information:

Source of variance	Sum of squares	Degrees of freedom	Mean square
T	19,840	7	2830**
θ	69,770	9	7750**
$T\theta$	2,620	63	200**
Error	425.8	80	5.3

The nature of the test is such that only the highly significant treatment effect is of major interest. The method of least significant differences shows no significant effect from top to yarn, although the mean for roving is slightly higher than that for yarn. This condition is the only one that is inconsistent with the Pauly test and expected results. Otherwise, processing produces a strong increase in dye susceptibility and steaming does the opposite. The inconsistencies may result from the disturbance of the normal pattern of progressive surface modification by the interspersed steamings or inadequate control of sample weight when sample conditions are nearly equal as a result of processing history.

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The Swelling of Human Hair in Water and Water Vapor*

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Abstract

Data are presented on the swelling of free and strained hair fibers in water and water vapor. The strained hair fibers were either under constant load or at constant elongation. In some cases rates of swelling are also shown. The swelling isotherms of the free fibers follow the volume changes predicted from density measurements (for wool) except at very high relative humidities. Straining the fiber may either increase or decrease the amount of swelling, depending on the type of experiment. An attempt to develop a statistical mechanical model to explain the equilibrium absorption and swelling behavior of a hair fiber is only partly successful. Finally, there seems to be evidence from the rates of swelling to indicate inhomogeneities in the hair with respect to its response to mechanical deformations.

Introduction

In a previous paper [16], which hereinafter is referred to as "part I," the authors presented and discussed data on the swelling of single human hairs, unstressed and under small constant loads, as a function of the relative humidity of the surrounding air. The purpose of the present paper is to present further results of the study of the swelling of hair in water vapor. These results can be grouped into the following four sections: (1) further swelling data for single fibers under very small loads measured in part under greatly improved experimental conditions; (2) data on swelling at constant elongation over a much greater range of elongations than can be obtained at constant load without serious creep effects; (3) data on rates of swelling; (4) correction and extension of the theoretical treatment of absorption and swelling given in part I.

It should be emphasized that these data are swelling data and not adsorption data. They are of interest in themselves since they demonstrate certain facets of the general nature of water absorption by hair—in particular, its anisotropic character. For this reason, longitudinal and diametral swelling measurements are as important as volumetric measurements. The volumetric degree of swelling is obviously closely connected with the amount of water absorbed, but the quantitative interrelationship has not yet been worked out. This relationship is examined in this paper for the case of fibers which are not under tension. For reasons which are primarily experimental and are discussed later, only a rough approximate rule of additivity of specific volumes can be justified experimentally at the present time. In the case of fibers under tension, since the tension can affect the specific volumes of each component as well as the relative proportions of each, more data are necessary before even a rough experimental relationship can be obtained. In this connection it might be mentioned that regain and density data taken in the conventional way are essentially averages of the values for many single fibers. To minimize fiber-to-fiber variations, swelling data on as many fibers as possible should be used for purposes of comparison.

Using additivity of specific volumes as an empirical rule and the swelling data of part I, we predicted a decrease in the amount of water absorbed with an increase in tension on the fiber. Treloar [15] found an increase in the amount adsorbed with increasing tension by direct measurement in a quite similar experiment. Furthermore, as Treloar pointed out and

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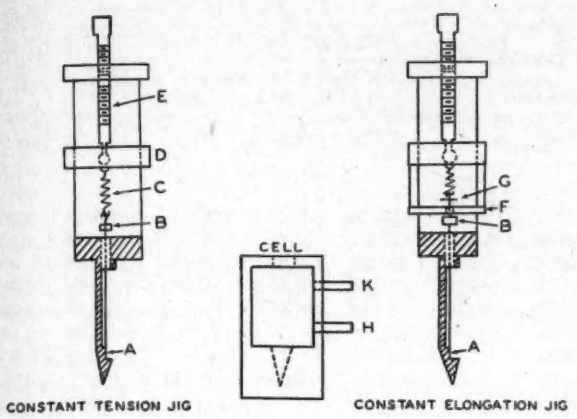

FIG. 1. *Diagram of the adsorption cell.*

as discussed later in this paper, there are general thermodynamic reasons for expecting an increase. It is thus possible that some of the swelling data—in particular, those involving fibers under very small stresses—are not representative of thermodynamic equilibrium. They are presented because we feel that they are the best data of this type available at the present time and because the apparent contradiction may be indicative of the influence of some secondary process of practical importance.

A theoretical isotherm is given which can explain (within its assumptions, one of which is additivity of specific volumes) most of the observed swelling and absorption data qualitatively. In particular, it offers a possible way to introduce the observed anisotropic effects. It cannot explain any swelling decreases with increasing tension, and does not fit the data for load-free hairs and hairs at constant elongation with the same set of constants.

Experimental Procedure

Microscopic swelling measurements (radial and axial) were made on 2- to 3-cm. lengths of human hair. The samples were mounted either under constant load or at constant elongation in a cell at a constant humidity. The hairs had a dry diameter of 40-60 μ, and were selected to have a ratio of major to minor axis of less than 1.10. The hairs were solvent-extracted, dried, mounted, and conditioned with a flow system using either sulfuric acid solutions or saturated salt solutions. Further details on sample selection, pretreatment, humidification, and statistical treatment of data are given in previous work [12, 16].* (The standard deviation of the mean is shown in the figures in most cases.)

Since the experimental techniques involved were in process of development while the work was being done, not all measurements were carried out in the same cell. Some were made in the cell described in part I, others in a different cell (shown in Figure 1). This cell was mounted vertically in the microscope to make better tension control possible ($\pm$ 0.01 g.). The working distance from fiber to objective was reduced to allow use of an 8-mm. objective giving a total magnification of about 260 $\times$, and the design permitted measurement of the diameter at two profiles differing by a rotation of 90°. It can be shown that, for an elliptical cross section of eccentricity less than 1.10, the maximum error introduced into the calculation of the cross-sectional area, by using any two perpendicular diameters obtained in this way as the major and minor diameters of the ellipse, is about 0.5%. Twenty spots for each profile of the fiber were followed throughout the measurements to minimize errors caused by irregularities (such as tapering) along the length of the fiber.

The cell consists of the cell proper, shown in the center of Figure 1, and a jig on which the fiber is mounted. The design of the jig depends in part on the type of experiment desired. Jigs for constant tension and constant elongation are shown.

The point of the jig fits into the slot in the bottom of the cell to form a conical thrust bearing. The fiber is mounted along the vertical axis of the jig so that rotation does not displace it horizontally, and the supporting arm of the jig is cut away as much as possible to allow measurements of two profiles 90° apart. The fiber is fastened at point *A* by a clamp consisting of a small flat piece of Phosphor bronze fastened by a small screw to a flat surface on the jig. The other end of the fiber is fastened at *B* to a clamp consisting of two flat pieces of Phosphor bronze, one of which is cut to form a hook, held together by a screw.

For the constant tension jig, the tension is provided by the spring, *C*, controlled by the screw, *E*, and movable collar, *D*. For the constant elongation jig, the weak spring can extend only a few millimeters before being stopped by the collar, *F*, and the stop, *G*, after which the elongation is determined by the

* We wish to thank Professors J. C. Whitwell and J. W. Tukey of Princeton University for help in the statistical treatment.

TABLE I. HUMAN HAIR—DIAMETER CHANGE $\left(\frac{\Delta D}{D_o}\right)$

(LOAD, 1 GRAM)

Sample → R.H. (%)	9	9A	11	12	14(1)	14(2)	21	19	40(1*)	40(2*)	Average
10	(0.025)	0.025	0.054	0.010	0.030	0.026	0.015	0.024	0.014	0.013	0.023 ± 0.004
40	0.057	0.043	0.072	0.029	0.075	0.068	0.028	0.067	0.030	0.037	0.051 ± 0.006
60	0.063	0.057	0.110	0.044	0.101	0.083	0.042	0.086	0.047	0.056	0.069 ± 0.008
90	0.089	0.084	0.133	0.080	0.142	0.123	0.091	0.133	0.088	0.093	0.106 ± 0.007
100	0.142	0.115	0.171	0.116	0.164	0.147	0.132	0.156	0.115	0.128	0.139 ± 0.006
90	0.083	0.087	0.120	0.100	0.141	0.125					0.109 ± 0.009
60	0.062	0.061	0.079	0.054	0.109	0.086					0.075 ± 0.008
40	0.050		0.069	0.038	0.084	0.072			0.033	0.041	0.055 ± 0.007
10	0.020	0.021	0.042	0.016	0.040	0.030					0.028 ± 0.004
0	0.009	0.006	0.000	0.001	0.003	0.007					0.004 ± 0.002
Standard deviation	0.007	0.006	0.007	0.004	0.006	0.003	0.001	0.005	0.002	0.002	

* The two columns for hair sample 40 give data at two profiles for the same conditions.

TABLE II. HUMAN HAIR—LENGTH CHANGE $\left(\frac{\Delta L}{L_o}\right)$

(LOAD, 1 GRAM)

Sample → R.H. (%)	9	9A	12	14(1)	14(2)	21	19	40	Average
10	(0.0062)	0.0062	0.0061	0.0047	0.0094	0.0044	0.0038	0.0039	0.0056 ± 0.0007
40	0.0166	0.0158	0.0150	0.0105	0.0134	0.0099	0.0103	0.0115	0.0129 ± 0.0011
60	0.0179	0.0203	0.0180	0.0119	0.0150	0.0124	0.0120	0.0143	0.0153 ± 0.0013
90	0.0198	0.0214	0.0200	0.0144	0.0162	0.0141	0.0152	0.0168	0.0172 ± 0.0015
100	0.0231	0.0233	0.0230	0.0155	0.0166	0.0140	0.0157	0.0178	0.0186 ± 0.0016
90	0.0195	0.0216	0.0220	0.0141	0.0159				0.0186
60	0.0174	0.0193	0.0200	0.0121	0.0136				0.0165
40	0.0149	0.0170	0.0180	0.0106	0.0121				0.0145
10	0.0093	0.0134	0.0130	0.0067	0.0081				0.0101
0	0.0058	0.0095	0.0102	0.0035	0.0052				0.0068

TABLE III. HUMAN HAIR—VOLUME CHANGE $\left(\frac{\Delta V}{V_o}\right)$

(LOAD, 1 GRAM)

Sample → R.H. (%)	9	9A	11	12	14(1)	14(2)	21	19	40	Average
10	(0.060)	0.058	0.114	0.026	0.066	0.063	0.034	0.057	0.033	0.057 ± 0.009
40	0.135	0.104	0.160	0.075	0.168	0.157	0.068	0.150	0.082	0.122 ± 0.013
60	0.150	0.140	0.240	0.109	0.227	0.190	0.099	0.195	0.119	0.163 ± 0.017
90	0.208	0.200	0.287	0.191	0.323	0.282	0.207	0.308	0.205	0.246 ± 0.015
100	0.336	0.273	0.365	0.274	0.376	0.338	0.300	0.357	0.274	0.321 ± 0.014
90	0.195	0.206	0.262	0.236	0.320	0.286				0.251 ± 0.019
60	0.147	0.148	0.177	0.133	0.245	0.197				0.173 ± 0.017
40	0.118		0.154	0.096	0.188	0.162				0.130 ± 0.015
10	0.049	0.050	0.097	0.046	0.089	0.069				0.068 ± 0.009
0	0.024	0.022	0.007	0.012	0.010	0.019				0.017 ± 0.005
Standard deviation	0.014	0.012	0.014	0.008	0.012	0.006	0.002	0.010	0.004	

TABLE IV. HUMAN HAIR—DIAMETER CHANGE $\left(\frac{\Delta D}{D_o}\right)$

(LOAD, 0 GRAM, SAMPLES 17 AND 20; LOAD, 0.2 GRAM, SAMPLES 40 AND 41)

Sample → R.H. (%)	17	20	40*	41*	Average
10	0.020	0.026	0.018	0.013	0.019 ± 0.003
40	0.040	0.064	0.033	0.031	0.042 ± 0.008
60	0.055	0.078	0.048	0.051	0.058 ± 0.007
90	0.104	0.124	0.104	0.094	0.107 ± 0.002
100	0.128	0.147	0.124	0.106	0.126 ± 0.010
90	0.112			0.091	
60	0.072			0.060	
40	0.059		0.033	0.039	
10	0.035				
0	0.025		0.002		

* Calculated from $\left(\frac{\Delta ab}{(ab)_o} + 1\right)^{\frac{1}{2}} - 1$, where a and b are diameters measured at two perpendicular profiles.

TABLE V. HUMAN HAIR—LENGTH CHANGE $\left(\frac{\Delta L}{L_o}\right)$

(LOAD, 0 GRAM, SAMPLES 17 AND 20; LOAD, 0.2 GRAM, SAMPLES 40 AND 41)

Sample → R.H. (%)	17	20	40	41	Average
10	0.0048	0.0040	0.0043	0.0043	0.0044 ± 0.0002
40	0.0118	0.0118	0.0110	0.0103	0.0112 ± 0.0003
60	0.0140	0.0138	0.0140	0.0127	0.0136 ± 0.0006
90	0.0166	0.0162	0.0175	0.0155	0.0165 ± 0.0005
100	0.0166	0.0165	0.0180	0.0159	0.0168 ± 0.0005
90	0.0167				
60	0.0133			0.0139	
40	0.0129		0.0107	0.0107	
10	0.0061				
0	0.0025		0.0004	0.0014	

position of F alone. The spring is useful in determining the initial position of zero elongation.

The cell is conditioned through ports H and K, and the thin cover glasses are sunk in the face of the cell to bring the fiber within the focal length of the objective.

No major errors resulting from the use of the less elaborate cells of part I were noted. The type of cell used will be specified for each set of data.

Results and Discussion

Swelling Data Under Small Loads

Swelling isotherms have been measured for nine individual hairs from the same head under 1-g. load (Tables I–III). Tables I–VI give the averages of the experimentally observed diameter changes (9 samples), the length changes (8 samples), and the

TABLE VI. HUMAN HAIR—VOLUME CHANGE $\left(\frac{\Delta V}{V_o}\right)$

(LOAD, 0 GRAM, SAMPLES 17 AND 20; LOAD, 0.2 GRAM, SAMPLES 40 AND 41)

Sample → R.H. (%)	17	20	40	41	Average
10	0.046	0.058	0.040	0.031	0.044 ± 0.007
40	0.096	0.147	0.076	0.074	0.098 ± 0.017
60	0.130	0.180	0.112	0.118	0.135 ± 0.015
90	0.239	0.290	0.236	0.212	0.244 ± 0.017
100	0.294	0.337	0.281	0.238	0.288 ± 0.021
90	0.257			0.207	
60	0.165			0.137	
40	0.135		0.077	0.090	
10	0.077				

Average Volume Change

(load, 1 gram or less, all samples)

R.H. (%)	$\frac{\Delta V}{V_o}$
10	0.053 ± 0.006
40	0.115 ± 0.011
60	0.155 ± 0.013
90	0.245 ± 0.013
100	0.311 ± 0.012

calculated volume changes. The values at the extreme right of Tables I–VI are standard deviations of the mean diameter change for the several samples. The values at the bottom of Tables I and III are standard deviations of the mean diameter change for the individual samples under adsorption conditions.

All samples had the same pretreatment. Samples 9, 9A, 11, 12, 14, and 19 were measured by the methods of part I. Sample 14 was discussed in part I. In addition to the standard pretreatment, it had been loaded with 35-g. weight in dry air, which caused an extension of 2%. It was relaxed in water before isotherm 14(1) was obtained. Subsequently, this sample was carried through sorption isotherms under 5-, 2-, and 1-g. loads without intermediate relaxing. Sample 21 was measured in a vertical position at a higher magnification but still at only one profile. It had previously been loaded with a 9-g. load at 60% R.H. and then relaxed without load in water before these particular measurements were made. The two sets of data for sample 40 were measured in the cell described in this paper, and represent data measured at the same time at two profiles separated by 90°.

It is evident that the diameter changes for different fibers have a considerable range at the same humidity. Average diameter and length changes have been cal-

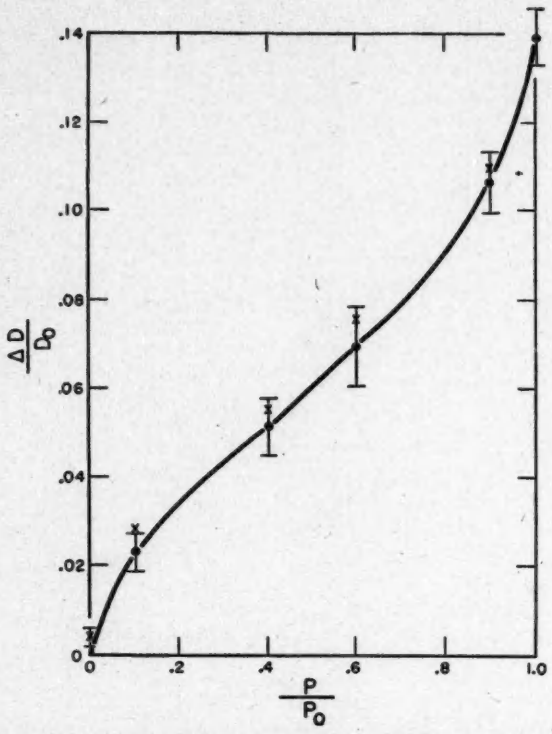

FIG. 2. *Diameter change of hair under 1-g. load as a function of relative humidity (average for 9 samples).* ●*—Adsorption.* ×*—Desorption.*

culated, and are plotted in Figures 2 and 3. Comparison with Figure 2 of curves for individual fibers plotted from the data in Table I shows that the large standard deviation of the average diameter changes is caused primarily by fiber-to-fiber variation.

Although the individual adsorption and desorption points are not significantly separated in Figure 2, in all cases the desorption points are higher than the adsorption points. The curves for the individual fibers almost invariably show this. As the technique was improved, and the standard error of the measurements decreased, the points for desorption lay consistently above those for adsorption. A Snedecor ratio of 20.4 was obtained for the adsorption and desorption points of samples 12, 14(1), and 14(2), indicating that for these samples the amount of hysteresis observed is very highly significant. It is evident that the hysteresis in length measurements is signficant at low humidities.

Data have also been taken under loads smaller than 1 g. The resulting diameter, length, and volume changes are given in Tables IV–VI, respectively.

FIG. 3. *Length change of hair as a function of relative humidity (average for 8 samples).* ●*—Adsorption.* ×*—Desorption.*

One profile of samples 17 and 20 was measured with the cell vertical and with the bottom end of the fiber (a very short sample) free. Two perpendicular profiles of samples 40 and 41 under loads of 0.2 g. were measured in the improved cell described above. This technique is much better than the method using a fiber with one end free, and hence the data are probably more reliable.

Comparison of Tables III and VI shows that the volume changes appear to be slightly smaller under effectively no load than under 1-g. load. The difference is always within the error of measurement of the readings except in saturated air (where difficulties in maintaining the relative humidity cause considerable error along the R.H. axis). Also, fiber-to-fiber variations can be of considerable importance in comparing two such small samples of data. Sample 19 in Table III and sample 20 in Table VI are consecutive samples from the same hair. The two runs marked 40 are consecutive runs on the same sample. This sample had also been loaded with 5 g. at 60% R.H. It was placed, load free, in water before use in this experiment. Comparison of these runs, which minimize fiber-to-fiber variation, shows no difference in swelling between the two tensions. Finally, we have measured the swelling on immersion in water under small tension for several more dry fibers, and have found 30%–32% to be the average swelling range. Thus, although the data given here indicate the possibility of a difference between the two tensions, if it exists, it is within the experimental error.

In addition to the use of direct microscopic measurements, the volume of the swollen fiber can be calculated if the regain and density of the fiber are

known as functions of the relative humidity. The usual methods for determining regain and density require measurements on samples composed of many fibers (the flotation method of measuring density can be used on single fibers, of course), and there are certain difficulties with each method. An interfiber capillary system exists in a bulk sample, which can lead to interfiber condensation at high relative humidities and hence to abnormally high values of regain. The density of a hair cannot be defined unambiguously since its experimental measure varies with the immersion fluid used. The difficulty really lies in the application of the concept of density to hairs, especially in fluids such as water. It has become a convention to accept the density of fibers, such as hair, measured in inert nonpolar organic liquids, such as benzene, as the nearest approximation to a classical density value. Bearing in mind these complications, the volume of the fiber-water system can be measured.

It is important to note that the density method does not distinguish between water adsorbed in capillaries and water dispersed throughout the system. The direct microscopic measurement does not measure water held in capillaries except in so far as the spreading pressure of such adsorbed films might distort the fiber, as suggested by Bangham [1] for charcoal. Thus, the direct measurement of volume change should be equal to or smaller than that derived from the density, and the difference between these, a measure of the amount of capillary adsorption.

We have attempted to compare our swelling data with values for wool derived using the density data of King [8]. We have recalculated King's volume changes using the regain data of Speakman [11], which seem superior to the regain data available to King. Although hair and wool are alike chemically, they differ in some respects physically, and it is not at all certain that they are quantitatively similar with respect to regain and density. In fact, Chamberlain and Speakman [2] report a 3% lower saturation regain for hair. However, Mellon, Korn, and Hoover [10] report regains for wool lower than those of Speakman, so that there may be no difference between hair and wool. Thus, there is some experimental uncertainty in the regain of hair and wool, especially at higher humidities. King does not give an estimate of the error in his density measurements. Judging from the scatter of his points, the standard deviation

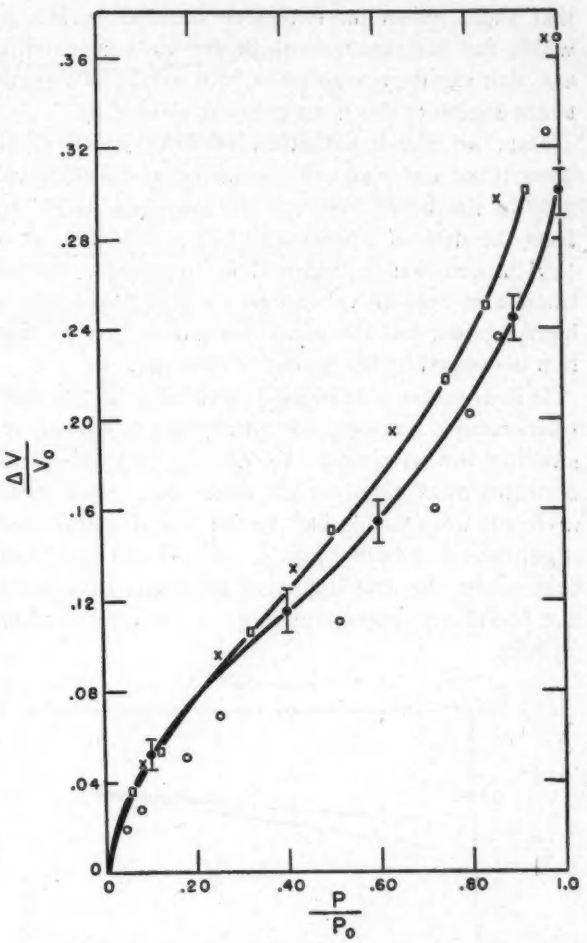

FIG. 4. *Volume change of hair as a function of relative humidity.* ×—*Calculated from the regain data of Speakman* [*11*], *assuming additive volumes.* ○—*Calculated from the density measurements of King* [*8*] *and the regain data of Speakman.* ●—*Calculated from direct microscopic diameter and length measurements under loads of 1 g. and less.* □—*Calculated from regain data of Mellon* et al. [*10*], *assuming additive volumes.*

of volume changes calculated from his data must be at least 0.4%.

In Figure 4, volume changes calculated from King's density measurements, and using Speakman's regain measurements, are compared with a curve prepared by averaging the data in Tables III and VI.

It is surprising that the volume changes derived from density measurements lie somewhat below those measured directly over most of the range of relative humidity. However, considering the probable limits of error in King's measurements, there is no real difference between the two measurements, at least until high humidities are reached. We can conclude

that there exists no extensive internal surface on which the hair can adsorb water without swelling, and that capillary adsorption, if it exists, is confined to the region of the isotherm near saturation.

Data for the hypothetical swelling which would occur if the water adsorbed contributed its molal volume in the liquid state to this swelling, calculated from the data of Speakman [11] and Mellon *et al.* [10], are shown in Figure 4 for reference. A contraction in over-all volume seems likely, especially at high regains, but the exact amount of this contraction is masked by the spread of the data.

It is apparent that precise knowledge of the interrelationships between the adsorption isotherm, the swelling isotherm, and the density requires measurements of all three on the same fiber. Such measurements are feasible but, to the best of our knowledge, have not been made as yet. Until they have been made, the assumption of additivity of volumes is a useful first approximation for the case of water on hair.

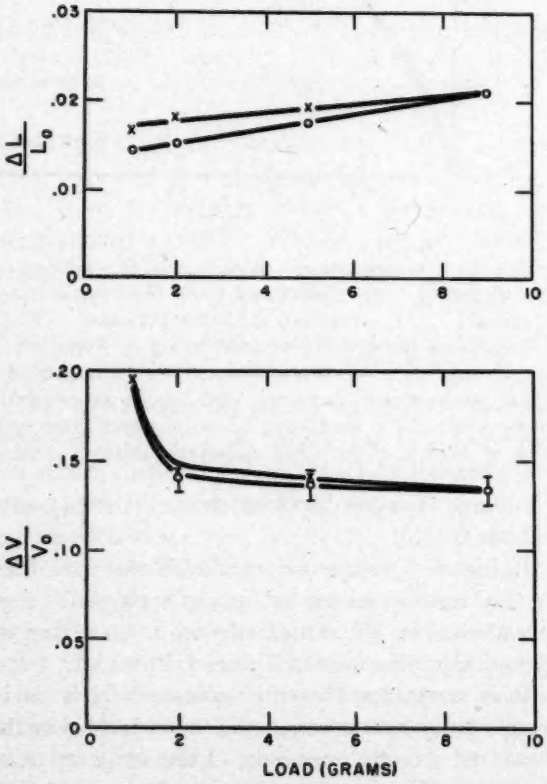

FIG. 5. *Length and volume changes of hair at 60% R. H. as a function of load* (L_0 = *length at 0% R. H., load 1 g.;* V_0 = *volume at 0% R. H., load 1 g.*). ○—*Extension.* ×—*Recovery.*

Swelling Under Tension

In part I, some preliminary results were presented on the effect of tension on the swelling isotherm. Sample 14 was carried through complete humidity cycles under successive loads of 1 g., 5 g., 2 g., and 1 g. An increase in tension on the fiber was accompanied by a rather large decrease in swelling, particularly in the middle range of humidities. At the completion of the experiment previously reported, the same sample, while under a 1-g. load, was again brought to 60% R.H., subjected to a loading cycle of 2 g., 5 g., 9 g., 5 g., 2 g., and 1 g., and the volume measured in each instance. The results are shown in Figure 5. A decrease in volume on extension is clearly evident. In Figure 6 the rate of change of diameter is shown for two of the changes in Figure 5. The length changes are practically instantaneous.

Figure 7 shows similar equilibrium data for five other hairs at various humidities. The lowest curve is that of Figure 5. In all cases the samples were elongated at a constant relative humidity and the volumes measured. The initial volume is that of the fiber under the smallest tension used and at the relative humidity of the experiment. A considerable fiber-to-fiber variation is noticeable.

The maximum elongation attained in Figure 5, using the length of the fiber under its lowest tension at the same relative humidity as a base, is about 0.5%. It is not possible to go to larger loads, at least at moderate or high humidities, without complications

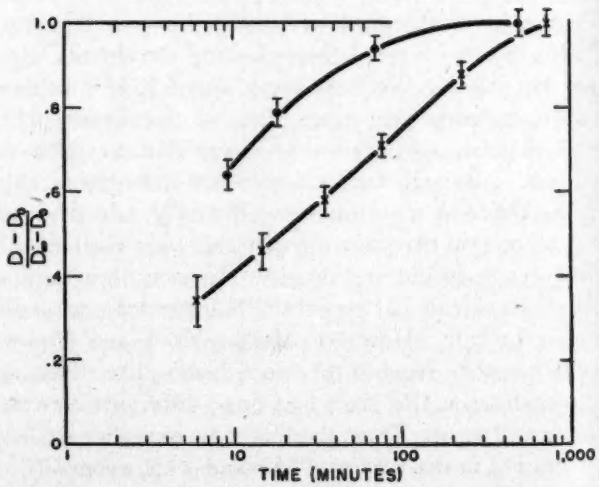

FIG. 6. *Rate of change of diameter of hair at 60% R. H. after a load change.* ●—*Change from 1 g. to 2 g.* ×—*Change from 2 g. to 1 g.*

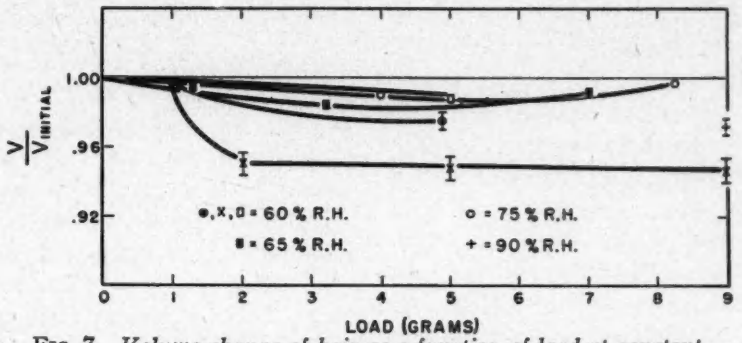

FIG. 7. *Volume change of hair as a function of load at constant relative humidity.*

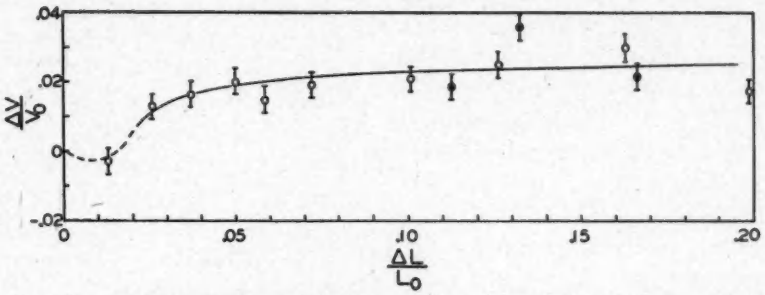

FIG. 8. *Volume change of hair as a function of elongation at 60% R. H.* ○*—Extension.* ●*—Recovery.*

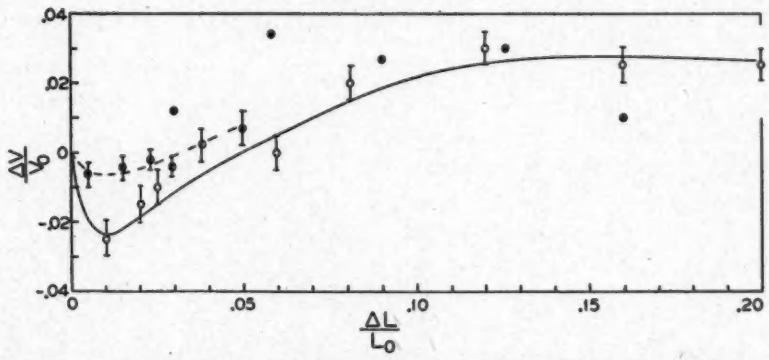

FIG. 9. *Volume change of hair as a function of elongation at 90% R. H.* ◐*—Extension, run 8.* ○*—Extension, run 1.* ●*—Recovery, run 1.*

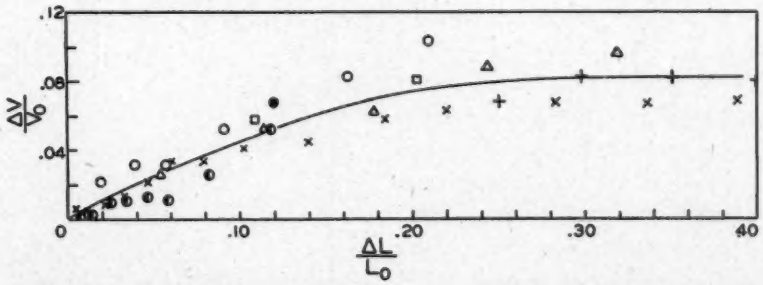

FIG. 10. *Volume change of hair as a function of elongation in liquid water.* ×*—Extension, run 12.* ◐*—Extension, run 14.* ○*—Extension, run 15.* △*—Extension, run 16.* □*—Extension, run 17.* +*—Recovery, run 12.* ●*—Recovery, run 15.*

arising from creep phenomena. Greater extensions can be obtained using the constant elongation jig described in this paper.

Figures 8, 9, and 10 show data taken using this jig at 60% and 90% R.H. and in liquid water. In these experiments the fiber is extended at constant relative humidity, and the volume of the hair measured. The values for the length and volume under a negligible load at the given relative humidity are the bases for plotting the volume change and the extension, a horizontal line cutting the ordinate at zero representing an elongation at constant volume. Figure 8 gives data on one hair, Figure 9 on two hairs, and Figure 10 on five hairs. In all cases, in the limit of large elongations there is a net increase in volume. In Figure 9 a decrease in swelling is noticeable at small extensions. It is possible that it occurs in Figure 8 also, particularly in view of the data presented in Figure 6. It should be noted that the smallest extension in Figure 8 is well beyond the largest in Figure 6. No decrease in volume occurred for any of the hairs averaged in Figure 10.

It is worth mentioning that the curves in Figures 8–10 are not completely reversible in the sense that a recovery history, the reverse of the extension history, will reproduce the volume curve from right to left over the whole range (see the recovery points on the figures). In particular, the original length is never recovered in a reasonable time after extensions greater than about 10%. This makes it entirely possible that these curves are not good approximations to equilibrium curves in the thermodynamic sense. Because of this, it may well be that the swelling behavior of hairs under tension is quite sensitive to the physical history of the hairs before use. We will give a further discussion of hairs under tension later.

It should also be pointed out that, since the fiber with its adsorbed water is a two-component system, either a change in the amount of water adsorbed or a change in density could account for the observed volume changes. The former would be expected for condensed phases, but regain measurements would be necessary to prove the point. (See Treloar's work [15] previously mentioned.) In this connection, King [9] found that wool stretched 20% at 70% R.H. showed a 1% increase in regain. The fibers were not weighed while stretched, but were weighed as quickly as possible after the load was removed. This qualitatively agrees with the results shown here.

Rates of Swelling

Figure 6 shows the rate of change of diameter following a change of load at a constant relative humidity. Figures 11–15 show the rates of change of the diameter and the length following a change of relative humidity, the load remaining constant. Data are given for two different loads, high and low humidities, and for adsorption and desorption. No effect of load is evident. The length appears to reach its equilibrium value more rapidly than the diameter for either adsorption or desorption.

For a fiber a few centimeters long and roughly 50 μ in diameter, the area of the sidewall is so much greater than the area of the ends that radial diffusion can be the only diffusion process of importance, especially when the ends of the fiber are clamped. There is thus a single unique diffusion process responsible for both types of swelling. However, radial diffusion into an anisotropic, swelling cylinder is a formidable theoretical problem which we are unable to solve. Nevertheless, we would like to make a few qualitative comments.

If the volumes of the fiber and the adsorbate are additive and if the length of the fiber remains constant, then the radius of the fiber, r, and the number of

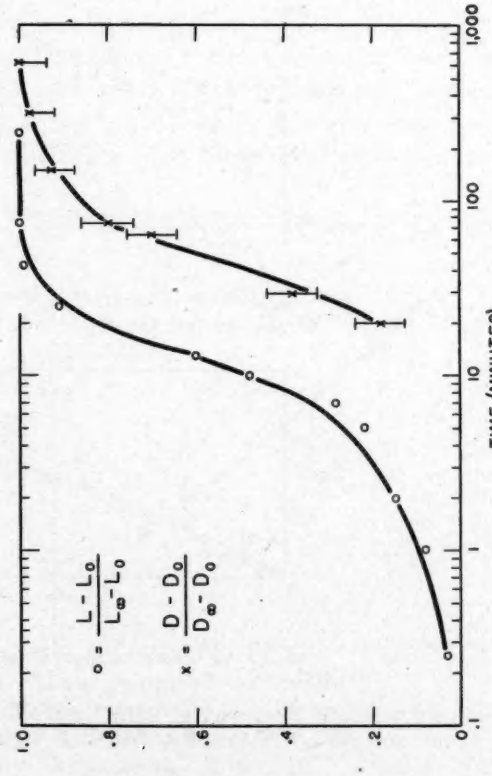

FIG. 11. *Load, 1 g.; R. H., 10% to 40%.*

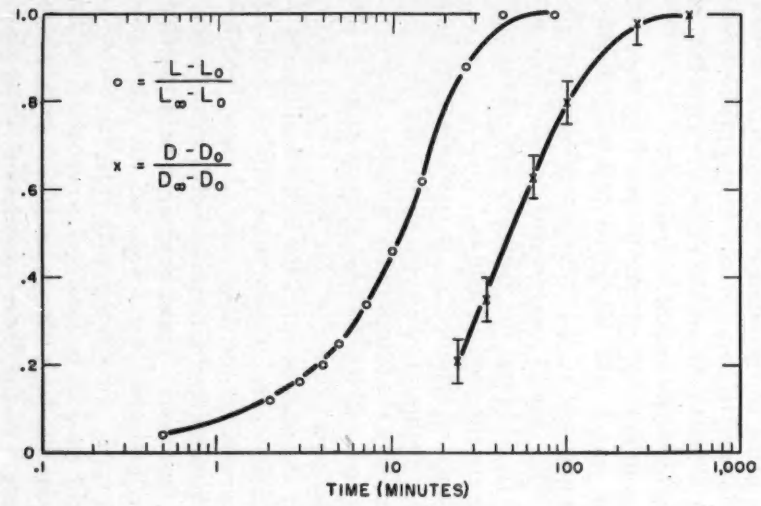

FIG. 12. *Load, 2 g.; R. H., 0% to 40%.*

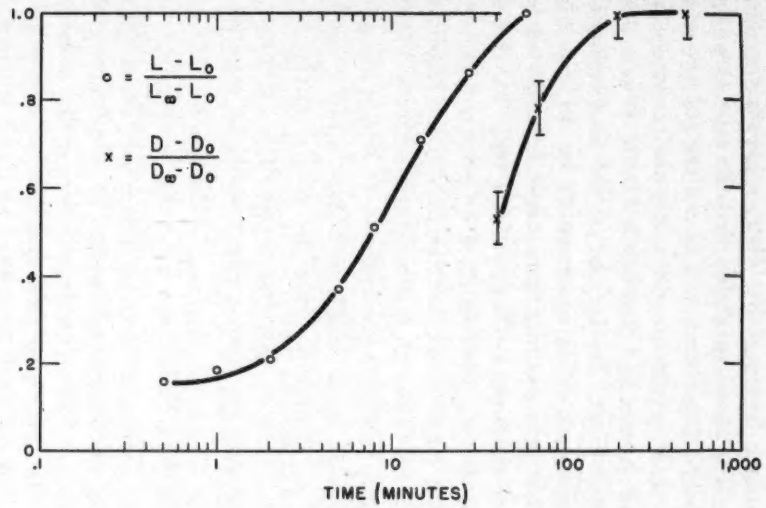

FIG. 13. *Load, 1 g.; R. H., 60% to 90%.*

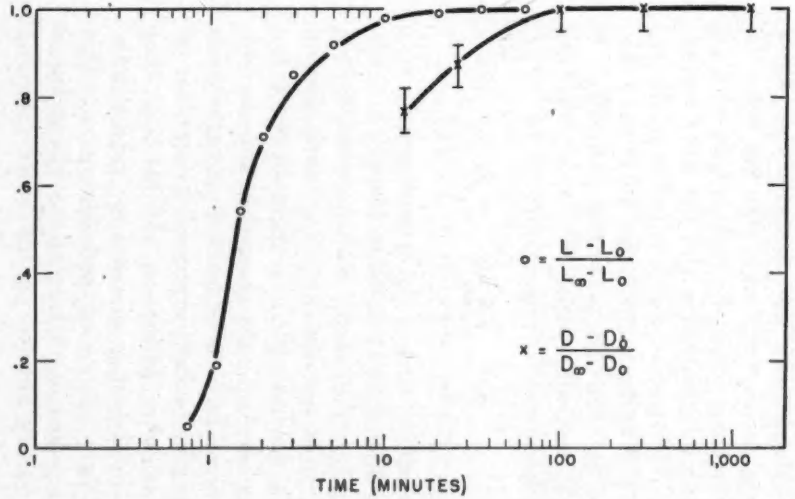

FIG. 14. *Load, 2 g.; R. H., 90% to 40%.*

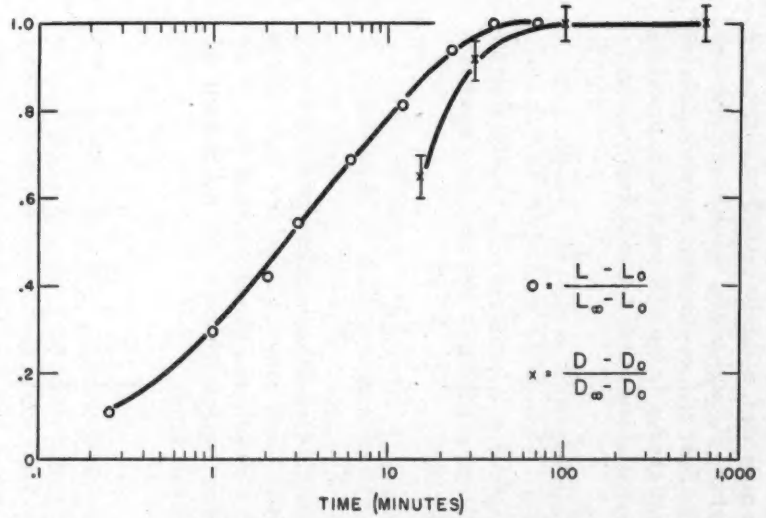

FIG. 15. *Load, 2 g.; R. H., 40% to 10%.*

FIGS. 11–15. *Rates of change of length and diameter of hair with changes of relative humidity at constant load.*

adsorbate molecules, n, can be related by $r^2 = (V_o + nv)/\pi l$, where V_o and v are, respectively, the volumes of the fiber and an adsorbate molecule, and l is the length of the fiber. For two values of n, n_1 and n_∞ (the subscript ∞ is used to denote a final value),

$$\frac{r^2 - r_o^2}{r_\infty^2 - r_o^2} = \frac{n_1}{n_\infty} = \frac{r - r_o}{r_\infty - r_o} \cdot \frac{r + r_o}{r_\infty + r_o}.$$

This expression is valid for either equilibrium or nonequilibrium conditions. For an anistotropic substance such that

$$\frac{r - r_o}{r_o} = K \frac{l - l_o}{l_o}, \quad (K \gg 1)$$

(which should be a good approximation for hair over a moderately small range of humidity below about 90% R.H.), substituting the above value for l in the expression relating the volume and the amount adsorbed, we can write

$$\frac{n_1}{n_\infty} = \frac{r - r_o}{r_\infty - r_o} \left[\frac{\left(\frac{r}{r_o} + 1\right) + \frac{1}{K}\left(\frac{r}{r_o}\right)^2}{\left(\frac{r_\infty}{r_o} + 1\right) + \frac{1}{K}\left(\frac{r_\infty}{r_o}\right)^2} \right]$$

for the equilibrium case. Since the fiber becomes saturated with adsorbate from the outside in, either the outer regions become longer than the inner regions or all regions retain the same length, with the outer regions in compression and the inner regions in tension. In this case, the distribution of the adsorbate, as well as the amount, may affect the external dimensions. We will ignore this possibility. If both r and r_∞ are within about 10% of r_o, either expression reduces, to a first approximation, to

$$\frac{n_1}{n_\infty} = \frac{r - r_o}{r_\infty - r_o}.$$

The fact that the form of the dependence of n on r is relatively insensitive to moderate changes in anisotropy strengthens the assumption that the equilibrium expression can be used for discussing nonequilibrium conditions in the second case without serious error.

Thus, the curves for the change of diameter with time in Figures 11–15 should be close approximations to the adsorption curves expressed as fractions of the final equilibrium adsorption. If this is so, then the change in elongation precedes the general mass change for both adsorption and desorption. This can be interpreted to mean that the elongation is disproportionately affected by the water taken up in the outer layers of the fiber, suggesting a skin effect. It is also a possibility that the rates at which the external dimensions of a fiber show the effect of increased or decreased adsorption are governed by the same factors that govern the rate of flow in different directions. In this case, if the fiber is physically anistotropic (as is known to be the case for hair), different swelling rates might be expected in different directions. There is little basis for choice between the two possibilities at the present time.

In part I and in the next section of this paper, a theory is developed for a homogeneous fiber in which the length changes are attributed to strong adsorption. Such a model might well show a rapid length change on adsorption, since the sites of strong adsorption could be expected to fill first. However, on desorption the reverse effect would be expected.

Theoretical Treatment

In this section we wish to correct and extend our previous theoretical treatment of the hair-water interaction. We are interested here in the adsorptive properties of hair both free and under tension. The treatment used consists of applying statistical mechanical methods to a simplified model chosen to have as many of the adsorptive properties of hair as possible and to conform, as a first approximation, to what is known about the molecular structure of hair and about molecular interactions.

The assumptions made are discussed, for the most part, in part I, and are given here very briefly. The assumptions of the statistical analogue of the simple BET theory, as derived by Hill [6], are made. In addition, the structure and changes of the hair are specified as follows.

The hair is assumed to be composed of long molecular chains, arranged parallel to the fiber axis and extending the length of the sample. However, we wish to avoid too detailed a specification of the molecular architecture of the hair. If, as seems likely at the present time, the individual chains in a keratin fiber exist in coils, these coils are assumed to be parallel to the fiber axis. Larger morphological features such as cortical cells are not considered, however. These chains are held together laterally primarily by forces of the hydrogen-bonding type. Interaction with external forces (to the extent we wish to consider) is accounted for by considering all chains to have the same length (which is the length of the fiber). Sites exist along these

chains on which water molecules can be strongly adsorbed, and the strong adsorption changes the physical properties of the chain in the immediate vicinity of the site. For simplicity, the unit of chain so involved will be called a "residue," and we will speak of "hydrated" and "unhydrated" residues. The secondary adsorption is assumed to occur between chains, and the volumes of the two systems (liquid-water and hair) are assumed to be additive. Finally, in considering the free-energy changes of the fiber phase caused by swelling, it is assumed that the swelling is purely radial in so far as the calculation of this term is concerned. Since radial swelling is considerably greater than axial swelling for hair, it can be expected that the most important term in the swelling free-energy change of the network is the radial term.

Let the basic unit of hair to be considered be 1 g. so that all extensive quantities are taken per gram of hair unless otherwise specified. Let A be the total number of residues per gram, and B the number of residues possessing primary adsorptive sites. A and B may or may not be identical. Let N be the number of chains, so that there are A/N residues per chain, etc. The force on the fiber is F, and α and x represent the total number of water molecules adsorbed and the number adsorbed on primary sites, respectively.

The partition function for a water molecule adsorbed on a primary site can be represented by q_1, where

$$q_1 = j_1 e^{\epsilon_1/kT}, \tag{1}$$

and where j_1 represents all terms referring to the localized motion of the adsorbed molecule and its internal degrees of freedom and ϵ_1 is the (negative) potential energy difference between the adsorbed molecule in its lowest state and an isolated gas molecule in its lowest state. The other terms have the conventional meanings.

The partition function, q_2, for a water molecule adsorbed on a secondary site can be written analogously as

$$q_2 = j_2 e^{\epsilon_2/kT}. \tag{2}$$

The partition function for an unhydrated residue under a force f can be written

$$q_4 = e^{-\frac{f^2 L_{01}}{2\psi_1 kT}}, \tag{3}$$

where L_{01} is the unstrained length of the residue and ψ_1 is the modulus of the residue. (It is assumed that the mechanical properties of the residue can be approximated by a simple spring.) It should be noted that here the force and the modulus are chosen per residue rather than per unit area, although the latter is the more conventional procedure.

Again, for a hydrated residue analogous definitions can be made and the partition function can be written

$$q_5 = e^{-\frac{f^2 L_{02}}{2\psi_2 kT}}. \tag{4}$$

Let the subscript i refer to the ith chain. Then, if x_i molecules of water are strongly adsorbed on the ith chain, the partition function for that chain, including the strongly adsorbed water, can be written:

$$Q_i = \frac{\left(\frac{B}{N}\right)!}{x_i!\left(\frac{B}{N} - x_i\right)!} q_1^{x_i} e^{-\frac{f^2 L_{01}}{2\psi_1 kT}\left(\frac{A}{N} - x_i\right)} e^{-\frac{f^2 L_{02}}{2\psi_2 kT} x_i}. \tag{5}$$

For given values of x_i for each chain, the part of the partition function concerned with primary adsorption is given by the product of these terms over the chains. For a given value of x, sums of these products must be taken subject to $\sum_i x_i = x$, where $x_i \leq B/N$, for all i, or

$$Q_x = \sum \prod_{i=1}^{N} Q_i. \tag{6}$$

The primary adsorption is now completely described. The secondary adsorption depends only on the value of x and not on the individual x_i's. Introducing secondary adsorption we have for given values of x and α

$$Q_{\alpha x} = Q_x \frac{(\alpha - 1)!}{x!(\alpha - x + 1)!} q_2^{(\alpha - x)} q_3(\alpha),$$

where the factorial term represents the configurational degeneracy (the number of ways $\alpha - x$ molecules can be adsorbed on x sites, with no restrictions on the number per site), the term in q_2 has been defined, and $q_3(\alpha)$ accounts for potential energy changes occurring in the hair as a result of the separation of the fiber molecules during swelling. It is obvious that on a localized basis this term varies with each of the configurational terms in the factorial. At this stage we will assume that it depends only on α, and will justify this assumption later.

Finally, removing the restriction of constant x, we get, for a given value of α,

$$Q_\alpha = \sum_{x=1}^{k} \left[\sum_{1}^{x_i} \left\{ \prod_{i=1}^{N} \frac{\left(\frac{B}{N}\right)!}{x_i!\left(\frac{B}{N} - x_i\right)!} \times q_1^{x_i} e^{-\frac{f_i^2 L_{01}}{2\psi_1 kT}\left(\frac{A}{N} - x_i\right)} e^{-\frac{f_i^2 L_{02}}{2\psi_2 kT} x_i} \right\} \times \frac{\alpha!}{x!(\alpha - x)!} q_2^{(\alpha - x)} \right] q_3(\alpha), \quad (7)$$

where $\sum_i x_i = x$ $\left(\text{where } x_i \leq \frac{B}{N}\right)$, and $k = \alpha$ (if $\alpha \leq B$) and $k = B$ (if $\alpha > B$) define the limits of x.

To proceed in a strictly statistical manner, we could imagine the fiber surrounded by fluid, the entire system under the appropriate mechanical constraints, with the total number of water molecules fixed. We could then sum the values of any property for which we want the average over all possible distributions of water molecules between the fiber and the fluid phases. This is not necessary, however, since the values of all properties essentially are determined by one particular distribution of water molecules between fluid and fiber phase, and this value is the average value. This distribution is the one which makes all the usual thermodynamic equations of equilibrium valid in the thermodynamic transcription of statistical mechanical equations. In other words, one particular value of the amount adsorbed, α, dominates the thermodynamic behavior of the system. Since the x_i's and x enter into the calculation in the same way that α does (as exponential factors), and since they are large numbers, sums over possible values of x and the x_i's will also be dominated by single terms, and these terms will preserve the validity of the statistical analogues of the classical thermodynamic equations.* It is shown in Appendix I, and it is perhaps intuitively obvious, that the average value of each x_i will be x/N, or, in other words, the strongly adsorbed molecules will be uniformly distributed over the chains for the type of experiment considered here. As a corollary of this, each f_i will be equal to f, where

$$f = F/N. \quad (8)$$

Equation (7) can now be rewritten as

$$Q = \frac{B!}{x!(B - x)!} \frac{\alpha!}{x!(\alpha - x)!} \times q_1^x q_2^{(\alpha - x)} q_3(\alpha) e^{-\frac{f^2 L_{01}}{2\psi_1 kT}(A - x)} e^{-\frac{f^2 L_{02}}{2\psi_2 kT} x}, \quad (9)$$

where $\frac{B!}{x!(B - x)!}$ has been substituted for

$$\left[\frac{\left(\frac{B}{N}\right)!}{\left(\frac{x}{N}\right)!\left(\frac{B}{N} - \frac{x}{N}\right)!}\right]^N,$$

to which it is approximately equal for large factorials.

It is now evident that any large inhomogeneities in the distribution of water molecules throughout the fiber are of negligible importance, so that the major contribution to the free energy from swelling the fiber will come from a uniform distribution. Since the volumes of water and hair are assumed additive, this means that this contribution will be independent of x and will depend only on α, as was assumed provisionally earlier.

If the length of the fiber is denoted by L, then we can write

$$L = \frac{AL_{01}}{N} + \frac{x}{N}(L_{02} - L_{01}) + \frac{AL_{01}f}{N\psi_1} + \frac{xf}{N}\left(\frac{L_{02}}{\psi_2} - \frac{L_{01}}{\psi_1}\right), \quad (10)$$

or, in terms of the elongation with respect to the dry unstressed fiber, l,

$$l = \frac{x}{AL_{01}}(L_{02} - L_{01}) + \frac{f}{\psi_1} + \frac{xf}{AL_{01}}\left(\frac{L_{02}}{\psi_2} - \frac{L_{01}}{\psi_1}\right). \quad (11)$$

Considering fixed quantities of fiber and water at a constant temperature, the thermodynamic condition for equilibrium can be written

$$\delta F = \delta W, \quad (12)$$

where δF represents any conceivable variation in the Helmholtz free energy, and δW the resulting work done by the surroundings on the system. The Helmholtz free energy of the system can be written $F = F^1 + F^2$, where F^1 and F^2 are the

*For a discussion, see Fowler [3] and Fowler and Guggenheim [4].

Helmholtz free energies of the fiber and fluid, respectively, and F^1 is given by $F^1 = -kT \ln Q$, where Q is given by equation (9).

We are interested in three cases: the free fiber, the fiber under a constant axial load, and the fiber at a constant elongation—all under constant fluid pressure.

Case I—The Free Fiber.—In this case, equation (12) can be written

$$\frac{\partial F^1}{\partial x}\delta x + \frac{\partial F^1}{\partial \alpha}\delta\alpha - \frac{\partial F^2}{\partial n^2}\delta\alpha = -P\left(\frac{\partial V^1}{\partial \alpha} - \frac{\partial V^2}{\partial \alpha}\right)\delta\alpha, \quad (14)$$

where n^2 is the number of water molecules in the fluid, so that $\delta\alpha = -\delta n^2$. Ignoring $P\frac{\partial V^1}{\partial \alpha}$ as negligible, equation (14) gives the two equations

$$\begin{aligned} \frac{\partial F^1}{\partial x} &= -kT\frac{\partial \ln Q}{\partial x} = 0 \\ \frac{\partial F^1}{\partial \alpha} &= -kT\frac{\partial \ln Q}{\partial \alpha} = \mu, \end{aligned} \quad (15)$$

where μ is the chemical potential of the water in the fluid phase. The treating of x as an independent variable follows from the discussion of equation (7). Performing the indicated differentiations we get

$$(B - x)(\alpha - x) = \beta x^2$$

$$\ln\frac{\alpha - x}{\alpha} + \eta v_2^{\frac{1}{3}} - \ln q_2 = \frac{\mu}{kT}, \quad (16)$$

where $\beta = q_2/q_1$, η is a constant, and v_2 is the volume fraction of fiber in the fiber phase. The term $\eta v_2^{\frac{1}{3}}$ arises from q_3 and represents the work done in swelling the fiber. It was discussed in part I, and a brief further discussion is given in Appendix II. If the liquid state is introduced as a reference state, and if the usual BET assumption is made that $q_2 = q_{\text{liq.}}$, where $q_{\text{liq.}}$ is the partition function for the liquid state, the isotherm (equations (16)) can be written

$$(B - x)(\alpha - x) = \beta x^2$$

$$\ln\frac{\alpha - x}{\alpha} + \eta v_2^{\frac{1}{3}} = \ln\frac{p}{p_0}, \quad (17)$$

where p/p_0 is the relative vapor pressure of the water at the given temperature. These equations are identical with those of part I.

*Case II—Fiber Under Constant Load.**—In this case, by equation (8), f is a constant, and work $F\,\delta L$ is done on the fiber. By substituting into equation (12), we get

$$\frac{\partial F^1}{\partial x}\delta x + \frac{\partial F^1}{\partial \alpha}\delta\alpha - \frac{\partial F^2}{\partial n^2}\delta\alpha = P\frac{\partial V^2}{\partial n^2}\delta\alpha + F\left[\frac{L_{02} - L_{01}}{N} + \frac{f}{N}\left(\frac{L_{02}}{\psi_2} - \frac{L_{01}}{\psi_1}\right)\right]\delta x, \quad (18)$$

where equation (10) has been used to evaluate δL. Carrying out the indicated differentiations and setting the coefficients of δx and $\delta\alpha$ equal to zero, we get

$$(B - x)(\alpha - x) = \beta' x^2$$

$$\ln\frac{\alpha - x}{\alpha} + \eta v_2^{\frac{1}{3}} = \ln\frac{p}{p_0}, \quad (19)$$

where

$$\beta' = \beta e^{-\frac{f(L_{02} - L_{01})}{kT} - \frac{f^2}{2kT}\left(\frac{L_{02}}{\psi_2} - \frac{L_{01}}{\psi_1}\right)},$$

and the reference state for the water has again been changed to that of liquid water with the usual BET assumption concerning q_2. Equations (19) and (11) give a complete description of the equilibrium adsorption and swelling properties of the fiber under a constant load at a constant temperature. (This case could be more concisely treated using a generalized partition function [5].)

Case III—Fiber at Constant Elongation.—Equation (12) can be written

$$\frac{\partial F^1}{\partial x}\delta x + \frac{\partial F^1}{\partial f}\delta f + \frac{\partial F^1}{\partial \alpha}\delta\alpha - \frac{\partial F^2}{\partial n^2}\delta\alpha = P\frac{\partial V^2}{\partial n^2}\delta\alpha \quad (20)$$

with the auxiliary condition

$$\frac{\partial L}{\partial x}\delta x + \frac{\partial L}{\partial f}\delta f = 0. \quad (21)$$

Using an undetermined multiplier, λ, on equation (21), we derive the three conditions:

$$\begin{aligned} &(a) \quad \frac{\partial F^1}{\partial \alpha} - \frac{\partial F^2}{\partial n^2} = P\frac{\partial V^2}{\partial n^2}; \\ &(b) \quad \frac{\partial F^1}{\partial x} + \lambda\frac{\partial L}{\partial x} = 0; \\ &(c) \quad \frac{\partial F^1}{\partial f} + \lambda\frac{\partial L}{\partial f} = 0. \end{aligned} \quad (22)$$

From the first of equations (22), we obtain

$$\ln\frac{\alpha - x}{\alpha} + \eta v_2^{\frac{1}{3}} = \ln\frac{p}{p_0}, \quad (23)$$

* This case was incorrectly treated in part I.

making the usual assumption regarding q_2. Solving equation (22*c*) for $\lambda(\lambda = -fN)$, substituting into equation (22*a*), and using equation (11) to obtain a value of f in terms of x and l, we obtain

$$2kT \ln \frac{(B-x)(\alpha-x)}{\beta x^2} + \frac{\left(\frac{L_{02}}{\psi_2} - \frac{L_{01}}{\psi_1}\right)\left[l - \frac{x}{AL_{01}}(L_{02} - L_{01})\right]\left[l + \frac{x}{AL_{01}}(L_{02} - L_{01})\right]}{\left[\frac{1}{\psi_1} + \frac{x}{AL_{01}}\left(\frac{L_{02}}{\psi_2} - \frac{L_{01}}{\psi_1}\right)\right]^2} + \frac{\frac{2}{\psi_1}(L_{02} - L_{01})\left[l - \frac{x}{AL_{01}}(L_{02} - L_{01})\right]}{\left[\frac{1}{\psi_1} + \frac{x}{AL_{01}}\left(\frac{L_{02}}{\psi_2} - \frac{L_{01}}{\psi_1}\right)\right]^2} = 0. \quad (24)$$

Equations (23) and (24) are the adsorption isotherm. The force can be obtained from equation (11).

Equations (16) and (11) were shown in Part I to give a good approximation to the behavior of a free fiber. Equation (19) predicts an increase in amount adsorbed as the load increases at constant relative humidity and temperature if

$$\frac{f(L_{02} - L_{01})}{kT} + \frac{f^2}{2kT}\left(\frac{L_{02}}{\psi_2} - \frac{L_{01}}{\psi_1}\right)$$

is positive. This will be true, since $L_{02} > L_{01}$ by assumption, if ψ_2 is less than or not too much greater than ψ_1, which seems reasonable. If the reverse is true, the increased stiffness of the hydrated chains would be such that, under tension, an increased amount adsorbed would result in a contraction. In fact, there is reason to believe that this is a necessary thermodynamic relationship between elongation and swelling—*i.e.*, if adsorption causes elongation, then mechanical elongation increases adsorption. This may be seen in the following way. If the relative humidity is unchanged, the partial molal free energy of the water in the fiber is unchanged, or, using T, P, F and x (x = mole fraction water in fiber) as independent variables,

$$\frac{\partial \mu}{\partial T}dT + \frac{\partial \mu}{\partial P}dP + \frac{\partial \mu}{\partial F}dF + \frac{\partial \mu}{\partial x}dx = 0. \quad (25)$$

At constant T and P this can be written

$$\left(\frac{dx}{dF}\right)_{p/p_0} = -\frac{\left(\frac{\partial \mu}{\partial F}\right)_{T,P,x}}{\left(\frac{\partial \mu}{\partial x}\right)_{T,P,F}}. \quad (26)$$

If we define $G = E - TS + PV - FL$, then $dG = -SdT + VdP - LdF + \mu dn$, where n is the number of moles of water in the fiber. If n is a constant, x is a constant, if the number of moles of fiber does not change, or

$$\left[\frac{\partial}{\partial F}\left(\frac{\partial G}{\partial n}\right)_F\right]_x = \left(\frac{\partial \mu}{\partial F}\right)_{T,P,x} = \left[\frac{\partial}{\partial n}\left(\frac{\partial G}{\partial F}\right)_n\right]_F = -\left(\frac{\partial L}{\partial n}\right)_{T,P,F}. \quad (27)$$

Thus, we can write

$$\left(\frac{dx}{dF}\right)_{p/p_0} = \frac{\left(\frac{\partial L}{\partial n}\right)_{T,P,F}}{\left(\frac{\partial \mu}{\partial x}\right)_{T,P,F}}. \quad (28)$$

The denominator must necessarily be positive; hence, the sign of the axial change on swelling determines the sign of the rate of change of x with F. (See in this connection the work of Treloar [13, 15] and Hill [7].)

Equations (23) and (24) show the same type of dependence of volume on elongation as is experimentally shown in Figure 10 and in the upper parts of Figures 8 and 9. However, the constants B and β, which must be used to fit the data in Figure 10, for example, are not those used in fitting the data for the free fiber. Using the constants taken from the free-fiber data gives a much smaller predicted increase in volume than is observed.

Thus, the theory provided in this section is capable of describing the gross features of adsorption and swelling phenomena for a free fiber and for a fiber held at various constant extensions in water. It cannot serve as a good approximation to both types of data simultaneously, however. It cannot provide an explanation for such data as are shown in Figure 7, or the small extension regions of Figures 8 and 9, or for the decreased swelling with increased load over the entire range of relative

humidities shown in part I.* The thermodynamic reasoning in this section casts doubt as to whether these last data can be true equilibrium data for a simple homogeneous substance. All points are practical equilibrium points (rate of change below the error of measurement) and are sometimes approachable from either side over a small region. However, mechanical and adsorptive hysteresis are known to occur in hair, which is a complex structure morphologically. It may be necessary to appeal to some factor in the morphology or the mechanical history of the fiber to explain certain effects. This possible complexity makes it all the more important to measure changes in amount adsorbed as well as changes in swelling.

Conclusions

It is interesting to compare the behavior of hair in water vapor with the much better understood behavior of lightly cross-linked rubbers in such substances as benzene.†

The volumes of rubber and liquid benzene are additive to a very good approximation. The swelling of rubber in benzene is markedly affected by mechanical straining—in particular, extension in one direction causes a marked increase in swelling. To a good approximation the results may be interpreted in terms of the mixing of liquid molecules with polymer segments and the distortion of the polymer network.

For hair and water vapor, where both have been measured, swelling follows adsorption closely but not exactly, a net decrease in total volume being noted when the swollen fiber is compared with the dry fiber and liquid water. At larger elongations the swelling increases, but not in exactly the same way as, and to a much lesser degree than, in rubbers. At smaller elongations and under moderately small constant loads decreases in swelling can be observed. In addition, anisotropic effects and large heat changes occur which do not occur with rubber. An attempt to interpret the data for hair in terms of a BET adsorption throughout a deformable network designed to show the proper anisotropy was only partly successful. In particular, the observed decreases at smaller elongations or under moderate loads could not be interpreted even qualitatively.

If swollen rubber in equilibrium with benzene is thought of as a compressible material in the sense that it can gain or lose benzene, then any strain, the stresses for which can be analyzed into a system having a component of hydrostatic tension, will cause an increase in swelling [13]. Applying the same reasoning to hair in water, the same effects might be expected, lessened because of the large heats of interaction between hair and water. In addition, a specific anisotropic hydration effect such as is postulated in the theory developed in this paper may be important. This theory of behavior is attractive in the case of keratin fibers because of their apparent coiled molecular structure. It seems reasonable that primary adsorption of a water molecule would cause the coil to open somewhat. For fibers such as those composed of cellulose, the way in which primary adsorption could cause expansion along the molecular chain, and hence account for swelling anisotropy and in part for the effects of tension, is vaguer, and hence the theory is less appealing.

Finally, the possible importance of morphological and hysteretic factors should not be overlooked. Hair fibers are kown to possess a cuticle or skin-like outer membrane, and it would not be surprising if this outer layer exerts a dominant influence on some of the mechanical responses of the hair, as is suggested by the rate-of-swelling data shown here. Adsorption hysteresis is also well known and may play an important part, particularly with respect to the response to mechanical deformation.

Appendix I

Here we wish to examine in further detail the assumption that the largest contribution to the free energy is made by the terms representing uniform distribution of the strongly adsorbed molecules among the chains.

Considering first constant elongation, the length of any chain can be written

$$L_i = \frac{AL_{01}}{N} + x_i(L_{02} - L_{01}) + \frac{AL_{01}}{N\psi_1} f_i + x_i f_i\left(\frac{L_{02}}{\psi_2} - \frac{L_{01}}{\psi_1}\right), \quad (29)$$

and, by assumption, this equals the length of the

* It was incorrectly stated in part I that such a model could explain these results theoretically.

† See Treloar [14] for results and references to earlier work.

fiber, L. Equation (7) can be written

$$Q = \left[\prod_{i=1}^{N} \frac{\left(\frac{B}{N}\right)!}{x_i!\left(\frac{B}{N} - x_i\right)!} \times q_1^{x_i} e^{-\frac{f_i^2 L_{01}}{2\psi_1 kT}\left(\frac{A}{N} - x_i\right)} e^{-\frac{f_i^2 L_{02}}{2\psi_2 kT} x_i} \right] \times \frac{\alpha!}{x!(\alpha - x)!} q_2^{(\alpha - x)} q_3(\alpha), \quad (30)$$

where α, x, and the values of the x_i's are the average values which dominate the thermodynamic behavior of the system. Since, at constant extension, each f_i is a function of the corresponding x_i only and $\sum_i x_i = x$, Q is a function of the x_i's, α, and T only. At constant temperature the equilibrium condition can be written

$$\delta F = -kT\,\delta \ln Q = 0. \quad (31)$$

Since Q is symmetrical in the x_i's, this equation will require that every x_i have the same value, which will necessarily be x/N.

For a constant load on the fiber, in addition to equation (30), we have the auxiliary conditions

$$\sum f_i = F$$

$$\pi f_i + \sigma x_i f_i + s x_i + r = \pi f_1 + \sigma x_1 f_1 + s x_1 + r \quad (32)$$

for all i, where

$$\pi = \frac{AL_{01}}{N\psi_1}, \qquad \sigma = \left(\frac{L_{02}}{\psi_2} - \frac{L_{01}}{\psi_1}\right),$$

$$s = L_{02} - L_{01}, \qquad r = \frac{AL_{01}}{N}.$$

Here chain 1 has been arbitrarily selected as a standard of reference. Using the thermodynamic condition

$$\delta F = -kT\delta \ln Q = \delta W \quad (33)$$

and undetermined multipliers λ_1 and λ_i ($i \neq 1$), we obtain the set of equations

$$\frac{\partial \ln Q}{\partial x_1}\delta x_1 + \frac{\partial \ln Q}{\partial f_1}\delta f_1 + \cdots + \frac{\partial \ln Q}{\partial x_i}\delta x_i + \frac{\partial \ln Q}{\partial f_i}\delta f_i + \cdots$$
$$= \left[-\ln x_1 + \ln\left(\frac{B}{N} - x_1\right) + m f_1^2\right]\delta x_1 + [-2f_1(n - m x_1)]\delta f_1 + \cdots$$
$$+ \left[-\ln x_i + \ln\left(\frac{B}{N} - x_i\right) + m f_i^2\right]\delta x_i + [-2f_i(n - m x_i)]\delta f_i + \cdots$$
$$= F\delta L = F[(\pi + \sigma x_1)\delta f_1 + (s + \sigma f_1)\delta x_1], \quad (34)$$

where

$$m = \frac{1}{2kT}\left(\frac{L_{01}}{\psi_1} - \frac{L_{02}}{\psi_2}\right), \qquad n = \frac{L_{01}\left(\frac{A}{N}\right)}{2\psi_1 kT};$$

and

$$\lambda_1 \sum \delta f_i = 0$$

$$\lambda_i[(\pi + \sigma x_i)\delta f_i + (\sigma f_i + s)\delta x_i - (\pi + \sigma x_1)\delta f_1 - (\sigma f_1 + s)\delta x_1] = 0, \quad (35)$$

for $i \neq 1$. There are $N - 1$ of these last equations. Setting coefficients of different variations equal to zero and using the ith chain as an example,

$$-\ln x_i + \ln\left(\frac{B}{N} - x_i\right) + m f_i^2 + \lambda_i(\sigma f_i + s) = 0 \quad (36)$$

$$-2f_i(n - m x_i) + \lambda_1 + \lambda_i(\pi + \sigma x_i) = 0. \quad (37)$$

From the condition that all chains have the same length, we get

$$f_i = \frac{\theta - s x_i}{\pi + \sigma x_i}, \quad (38)$$

where

$$\theta = \pi f_1 + \sigma x_1 f_1 + s x_1. \quad (39)$$

Equations (36), (37), and (38) may be combined to give

$$\lambda_1 = \frac{2(\theta - s x_i)(n - m x_i)}{\pi + \sigma x_i} - (\pi + \sigma x_i)\left[\frac{\ln x_i - \ln\left(\frac{B}{N} - x_i\right) - m\left(\frac{\theta - s x_i}{\pi + \sigma x_i}\right)^2}{\sigma\left(\frac{\theta - s x_i}{\pi + \sigma x_i}\right) + s}\right]. \quad (40)$$

This is true of all x_i, where $i \neq 1$, and hence they are all equal. Since the choice of x_1 as a reference was arbitrary, it too is equal to the rest. Hence the average value of $x_i = \frac{x}{N}$, for all i, and $f_i = \frac{F}{N} = f$, for all i.

The case of the free fiber obviously is a special case of the fiber under a constant load.

Appendix II

We wish to develop the partition function for the swelling of a model consisting of a number of chains aligned along a common axis and held together laterally by electrostatic attractions of one type or another. The partition function for ξ pairs of attracting point charges separated by a distance r in a medium of dielectric constant K can be written

$$Q = e^{\frac{\xi|e_1e_2|}{KrkT}}. \tag{41}$$

For ξ pairs of dipoles of strengths p_1 and p_2 aligned so as to attract each other at a distance r, the partition function is

$$Q = e^{\frac{\xi|p_1p_2|}{Kr^3kT}}. \tag{42}$$

In each case, r is related to the diameter of the fiber, D, by $r = G(D - C)$, where G and C are constants. Since $D = D_o v_2^{-\frac{1}{2}}$ (ignoring the slight longitudinal swelling), where $v_2 = V_o/(V_o + \alpha)$, this can be written

$$r = A(D_o v_2^{-\frac{1}{2}} - C). \tag{43}$$

Solving for the partial molal free energy, for point charges,

$$\mu = \frac{\partial A}{\partial \alpha} = -kT\frac{\partial \ln Q}{\partial \alpha}$$

$$= \frac{\xi|e_1e_2|}{2KGD_oV_o}\frac{v_2^{\frac{1}{2}}}{\left(1 - \frac{C}{D_o}v_2^{\frac{1}{2}}\right)^2} \cong \eta v_2^{\frac{1}{2}}, \tag{44}$$

if $C \ll D_o$, where

$$\eta = \frac{\xi|e_1e_2|}{2KGD_oV_o}; \tag{45}$$

and for dipole-dipole interaction

$$\mu = \tfrac{3}{2}\frac{\xi|p_1p_2|}{KG^3D_o^3V_o}\frac{v_2^{\frac{5}{2}}}{\left(1 - \frac{C}{D_o}v_2^{\frac{1}{2}}\right)^4} \cong \eta' v_2^{\frac{5}{2}}, \tag{46}$$

if $C \ll D_o$, where

$$\eta' = \tfrac{3}{2}\frac{\xi|p_1p_2|}{KG^3D_o^3V_o}. \tag{47}$$

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The Geometry of Knit Fabrics Made of Staple Rayon and Nylon and Its Relationship to Shrinkage in Laundering

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Abstract

The geometry of six plain, six rib, and three interlock circular knit fabrics made of staple fibers of viscose, acetate-viscose, and nylon has been studied. Data on both gray and finished fabrics for stitch length, diameter of yarn, and wale and course spacings were used in evaluating the equations derived by Peirce for length of yarn in one stitch and for weight per unit area. Measured stitch length ranged from $l = 2p + w + 4.18d$ to $l = 2p + w + 6.74d$, as compared to the theoretical value of $l = 2p + w + 5.94d$ which Peirce derived. Weight of the fabrics calculated by Peirce's equation showed good agreement with that obtained by weighing a known area.

In laundering tests, it was found that the various yarns shrank or stretched less than 3% in the finished fabrics. The data of wale and course spacings of both the laundered gray and laundered finished fabrics followed parabolic curves. Curves relating the wale and course spacings of the unlaundered materials conformed to no orderly pattern. Those unlaundered materials in which wale and course spacings approximated the parabolic relationship of the laundered fabrics changed the least in the length and width dimensions. Shrinkage in area increased with knitting stiffness for all of the gray fabrics and for the finished viscose; but, for the finished acetate-viscose and nylon, shrinkage in area usually decreased as the knitting stiffness increased.

IN a previous paper [2] the present authors discussed the geometry of plain and 1 × 1 rib knit cotton fabrics and its relation to shrinkage in laundering. This research on the geometry of knit goods has been continued to include materials made of staple rayon and nylon. Interlock knitting, as well as plain and 1 × 1 rib knitting, has been included.

Materials

The fabrics studied were knit of three different yarns under controlled conditions in the Textile Research Department of the American Viscose Corporation. Yarns were 30/1 spun with approximately 18Z turns per inch from the following 1.5-in. staple fibers: (*1*) bright viscose, 1.5 denier; (*2*) blend of 50% dull acetate and 50% bright viscose, 2.0 denier; (*3*) bright nylon, 1.5 denier.

Plain and 1 × 1 rib fabrics were knit in 24, 28, 32, 36, 40, and 44 courses per inch; interlock fabrics, in 24, 28, and 32 courses per inch.

The circular machines used in knitting the plain, rib, and interlock fabrics were, respectively: (*1*) 28 cut, 20-in. diameter; (*2*) 12 cut, 18-in. diameter; (*3*) 24 cut, 20-in. diameter.

Some of the yardage of the gray goods was reserved for the study of unfinished goods. The remainder was scoured, bleached, and calendered. The nylon fabrics were first given a hot-water presetting treatment in order to prevent the formation of creases or cracks and to insure satisfactory finishing.

Method

Measurements were made of yarn number, diameter of yarn, stitch length, weight per square yard, and number of wales and courses per inch, as in a previous study of cotton knit goods [2]. These data were applied to Peirce's equations to determine whether or not they followed the theoretical relationships which he derived [4].

Data on dimensional change in laundering and on fabric properties were obtained for each material. Since there is no standard test method for measuring shrinkage in laundering for knit goods, the procedure used was the A.A.T.C.C. standard method for woven textiles at 100°F [1]. Three 15 in. × 15 in. spec-

TABLE I. WALE AND COURSE COUNT, STITCH LENGTH, AND WEIGHT OF FABRICS KNIT OF RAYON AND NYLON

Fabrics	Knitted courses per inch*	Counted wales and courses per inch: Gray Wales	Gray Courses	Finished Wales	Finished Courses	Length of stitch: Gray (.001 in.)	Finished (.001 in.)	Weight per square yard: Gray (calculated) (oz.)	Gray (experimental) (oz.)	Finished (experimental) (oz.)
Viscose										
Plain knit										
a	24	30.2	26.3	29.9	25.0	149.2	142.8	2.67	2.92	2.70
b	28	32.9	29.3	31.8	28.9	137.0	132.3	2.98	3.08	2.72
c	32	34.7	33.3	32.9	32.4	126.0	121.9	3.28	3.26	2.90
d	36	35.3	38.0	32.6	37.2	116.1	114.5	3.51	3.62	3.28
e	40	35.1	41.2	32.8	41.0	110.7	109.4	3.61	3.74	3.32
f	44	35.5	41.7	33.5	41.6	111.6	106.1	3.72	3.86	3.44
1×1 rib knit										
A	24	41.4	26.5	47.2	23.5	145.7	139.2	3.60	3.68	3.46
B	28	41.8	30.0	46.2	25.4	135.4	131.0	3.83	3.96	3.54
C	32	42.8	31.1	47.8	28.6	127.7	122.5	3.83	3.90	3.66
D	36	41.7	36.4	47.1	32.6	118.6	115.5	4.06	4.00	3.92
E	40	41.3	39.1	45.9	34.5	113.0	107.2	4.11	4.28	4.08
F	44	37.0	47.1	47.5	40.0	105.0	101.6	4.12	4.28	4.32
Interlock knit										
G	24	32.5	25.6	27.1	25.1	149.6	145.0	5.60	6.10	4.68
H	28	34.7	26.8	27.5	27.8	141.3	138.6	5.92	6.24	4.86
I	32	34.8	31.4	27.1	34.1	126.3	123.3	6.22	6.50	5.46
Acetate-viscose										
Plain knit										
a	24	31.5	26.3	32.7	23.1	150.1	148.3	2.68	2.90	2.62
b	28	32.3	29.2	33.8	25.6	142.0	138.2	2.89	3.24	2.80
c	32	34.1	32.0	33.4	30.2	128.4	127.2	3.03	3.26	2.92
d	36	35.5	36.9	33.5	34.7	117.1	116.2	3.31	3.46	3.00
e	40	36.3	41.3	35.7	39.5	110.4	105.9	3.57	3.76	3.38
f	44	36.0	45.8	36.0	41.6	106.8	101.9	3.80	3.90	3.66
1×1 rib knit										
A	24	41.2	27.6	41.5	24.0	143.2	140.1	3.52	3.72	2.96
B	28	44.9	27.7	39.1	26.4	135.9	135.1	3.65	3.80	2.96
C	32	46.1	31.2	44.1	28.0	129.5	126.5	4.02	4.30	3.32
D	36	43.5	36.4	39.1	32.8	120.0	118.3	4.10	4.24	3.44
E	40	41.1	38.8	33.5	42.9	115.9	114.2	3.99	4.24	3.80
F	44	40.9	45.2	37.6	52.8	110.2	107.2	4.40	4.46	4.58
Interlock knit										
G	24	38.0	26.1	32.5	24.9	144.0	141.1	6.17	6.48	5.08
H	28	34.8	30.3	33.5	27.2	133.3	133.8	6.07	6.64	5.46
I	32	36.1	32.0	33.7	31.8	127.0	124.5	6.34	6.76	5.98
Nylon										
Plain knit										
a	24	27.6	29.1	32.4	27.7	156.4	150.1	2.81	3.42	3.10
b	28	30.4	34.0	34.5	31.2	141.1	135.6	3.27	3.76	3.36
c	32	31.3	36.4	37.3	33.8	132.8	130.2	3.38	4.22	3.68
d	36	32.8	38.7	37.2	36.4	127.1	122.6	3.61	4.00	4.06
e	40	35.4	44.2	38.5	38.9	118.8	116.2	4.16	4.44	4.16
f	44	36.5	43.4	39.5	41.7	116.8	110.8	4.14	4.38	4.34
1×1 rib knit										
A	24	41.7	25.3	40.7	27.0	150.2	149.9	3.55	4.44	4.14
B	28	48.8	33.0	42.8	30.4	141.5	139.1	5.10	4.86	4.50
C	32	50.2	35.8	46.6	33.4	124.3	124.1	5.00	5.28	5.26
D	36	54.1	40.1	53.2	36.9	119.5	118.9	5.81	5.68	5.56
E	40	49.2	44.4	59.1	40.0	111.0	111.3	5.43	5.92	6.34
F	44	56.4	43.2	54.2	43.3	113.0	102.6	6.16	5.94	6.22
Interlock knit										
G	24	33.3	27.4	37.6	25.5	154.6	150.6	6.32	6.82	6.54
H	28	34.5	30.6	38.0	28.0	143.6	140.4	6.79	7.48	6.68
I	32	35.4	36.4	39.6	32.7	131.5	125.6	7.59	8.02	7.22

* Courses were counted with the gray fabric in a relaxed condition after removal from the knitting machine.

imens of each fabric were used for measuring dimensional change in laundering. After the last rinse the specimens, without distortion, were floated in water over a wire screen placed on the bottom of a tray. Both the fabric and screen were lifted from the tray. The fabric was not removed from the screen until dry.

Results and Discussion

Length of Stitch and Weight

The equations derived by Peirce for flat plain knitting are as follows:

(*1*) for the length of yarn, *l*, in a unit cell or in one stitch:

$$l = 2p + w + 6 \cdot \sqrt{4/\pi} \cdot \sqrt{g/\rho},$$

which can also be expressed as

$$l = 2p + w + 5.94d;$$

(*2*) for the weight, *W*, per unit area of cloth:

$$W = \frac{lg}{wp},$$

where p is the course spacing, w the wale spacing or width per wale, g the weight per unit length of yarn, ρ the yarn density, and d the diameter of yarn. These equations were applied to the plain knit fabrics made of the manufactured fibers the same as in the study of knit cotton fabrics [2].

These same equations were applied to the 1×1 rib knit, with l representing the length of yarn in one loop and w the reciprocal of the total number of wales per unit length on both sides of the cloth.

In applying the equations to the interlock fabrics, l represented the length of yarn in one loop and w the reciprocal of the number of wales per unit length on one side of the cloth. Since interlock can be regarded as a double cloth composed of two 1×1 rib fabrics, the weight was calculated by use of the equation

$$W = \frac{2lg}{wp}.$$

The data for length of stitch for the gray and finished knit fabrics are given in Table I. The relationship of stitch length to the wale and course spacings is shown in Figure 1.

In order to find stitch length in terms of the diameter of the yarns, the diameter was calculated from the weight as well as measured (see Table II).

The yarn densities used for these calculations were found by assuming that the ratio of yarn density to fiber density was the same as that for cotton. The specific volume of cotton yarn was taken as 1.1, as recommended by Peirce [3].

TABLE II. NUMBER AND DIAMETER OF YARNS

Yarn	Number* (cotton system)	Diameter (experimental)† (.001 in.)	Diameter (calculated)‡ (.001 in.)	Critical diameter** (.001 in.)
Viscose	30.43	6.901	6.453	5.020
Acetate-viscose	31.75	6.315	6.476	5.039
Nylon	30.62	7.892	7.429	5.780

* Mean of 10 determinations.
† Mean of 40 determinations.
‡ Calculated from yarn densities: viscose, 0.92; acetate-viscose, 0.86; nylon, 0.69.
** Calculated from fiber densities: viscose, 1.52; acetate-viscose, 1.42 (mean of 1.52 and 1.33); nylon, 1.14.

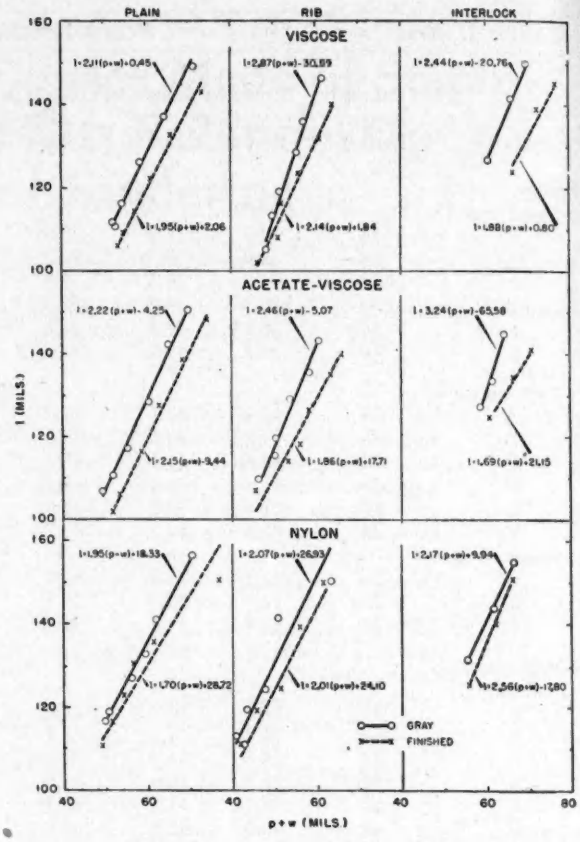

FIG. 1. *The relationship of stitch length or loop,* l, *to course and wale spacings,* p + w, *of gray and finished knit fabrics.*

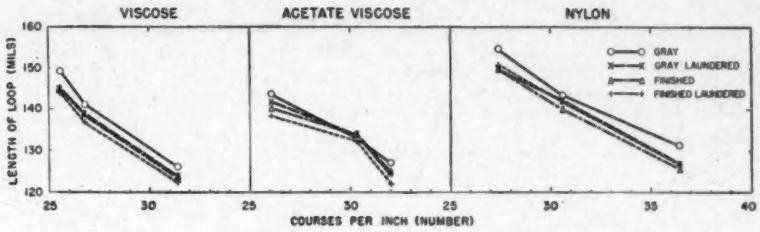

FIG. 2. *Length of loop before and after five launderings of interlock knit fabrics of various courses per inch.*

Stitch length of the fabrics was found to be approximately

$$l = 2p + w + 5.4d.$$

The data for l ranged from $2p + w + 4.18d$ to $2p + w + 6.74d$. These results agree closely with those given by Peirce's equation for stitch length [4].

For calculating the weight, the equation

$$W = \frac{24}{35}\frac{n_c n_w l}{N}$$

was used for the plain and 1×1 rib fabrics, and

$$W = \frac{48}{35}\frac{n_c n_w l}{N}$$

for the interlock fabrics. In these equations W is weight in ounces per square yard, n_c and n_w are the number of courses and wales per inch, l is the length of one loop in inches, and N is the yarn number in the cotton system. The calculated weight showed good agreement with that obtained by weighing a known area (see Table I).

Effect of Laundering

Stitch length.—Measurements of yarns raveled from the fabrics before and after laundering revealed that the shrinkage of the different kinds of yarns was small. Figure 2 shows the length of loop for gray and finished interlock fabrics before and after five launderings. Similar results were obtained for the plain and rib knit fabrics.

The stitch length of the plain, rib, and interlock gray fabrics decreased as much as 4% in five launderings for the viscose and nylon, and as much as 2.5% for the acetate-viscose.

In the finished goods the viscose yarn in the plain and rib knit fabrics stretched between 2% and 3% in laundering, but in the interlock fabrics it neither shrank nor stretched. The nylon yarn in the finished

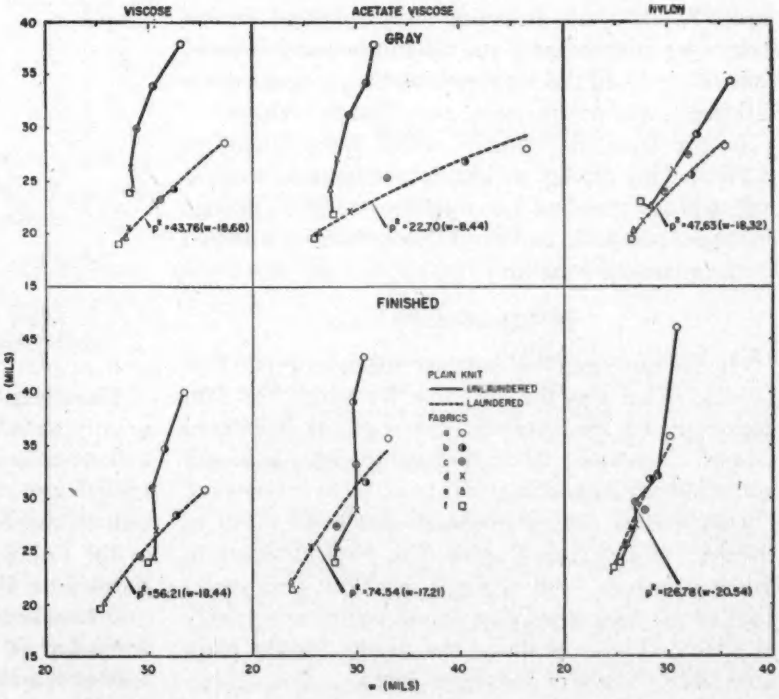

FIG. 3. *Wale* (w) *and course* (p) *spacings of plain knit fabrics before and after five launderings.*

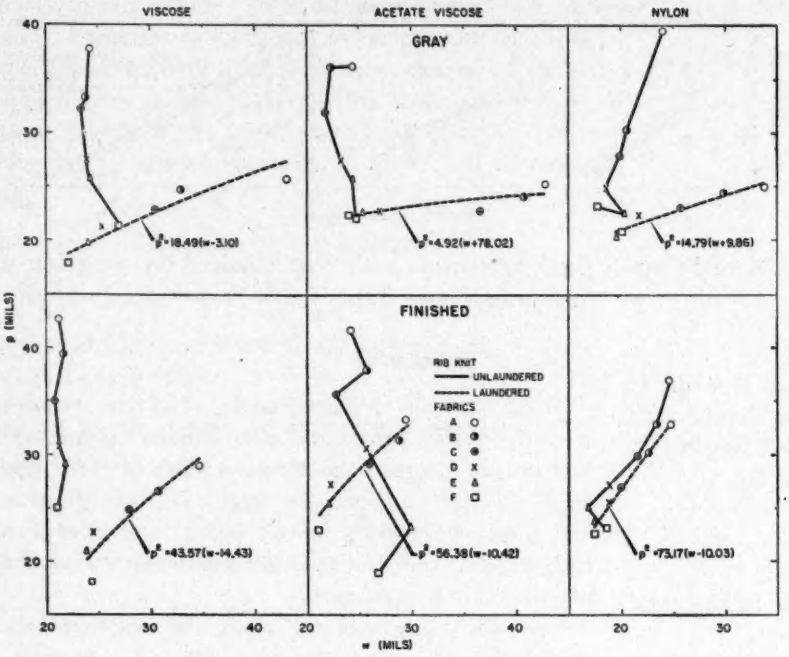

FIG. 4. *Wale* (w) *and course* (p) *spacings of rib knit fabrics before and after five launderings.*

fabrics showed only slight changes in laundering—less than 1% stretch or shrinkage. The acetate-viscose yarn shrank less than 2%.

Wale and course spacings.—The relationship of wale spacing to course spacing of the unlaundered fabrics, both gray and finished, was quite different from that for the laundered fabrics (Figures 3, 4, and 5). Marked distortion was apparent in the curves for both the gray and the finished unlaundered knit fabrics, and the wale spacing-course spacing relationship was not the same for all of the fabrics.

In the laundered fabrics, which were floated in water before drying in order to eliminate stresses and strains, the data for wale and course spacings followed parabolic curves. These data were fitted to the quadratic equation

$$p^2 = a\ (w + b).$$

Of the unlaundered finished plain and rib knit fabrics, nylon was the only one for which the data approximated the parabolic curve of the laundered fabrics. The nylon fabric changed the least in length and width in laundering.

Dimensional change in length and width.—All of the gray fabrics shrank more than 10% in length in five launderings. All of the loosely knit gray materials except the plain knit nylon stretched excessively in width. Figure 6 shows the results for the plain knit fabrics made of the three yarns.

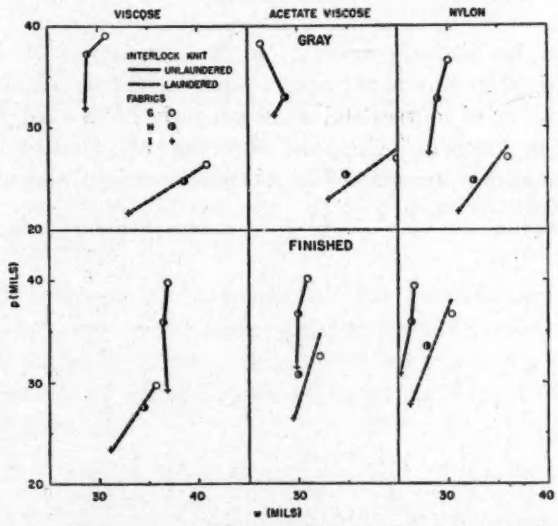

FIG. 5. *Wale* (w) *and course* (p) *spacings of interlock knit fabrics before and after five launderings.*

The excessive stretching in the width was usually greatly reduced by the finishing. Only the loosely knit viscose rib fabrics stretched more than 15%. Lengthwise shrinkage of the plain and rib knit materials in laundering was about the same in the gray as in the finished fabrics. However, finishing greatly reduced the length shrinkage of the interlock fabrics.

Dimensional change in area.—The trend in the relationship of the "cover factor," l/d, to change in area in laundering was the same for all of the gray

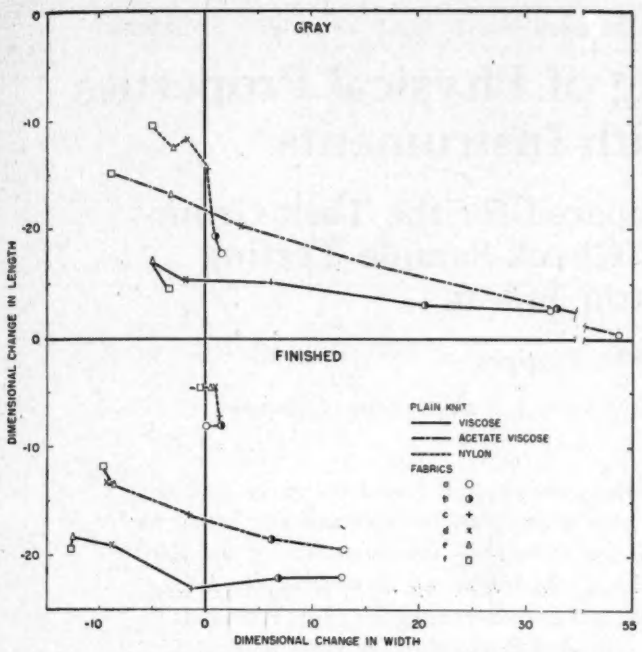

FIG. 6. *Dimensional change of length and width in five launderings of plain knit fabrics.*

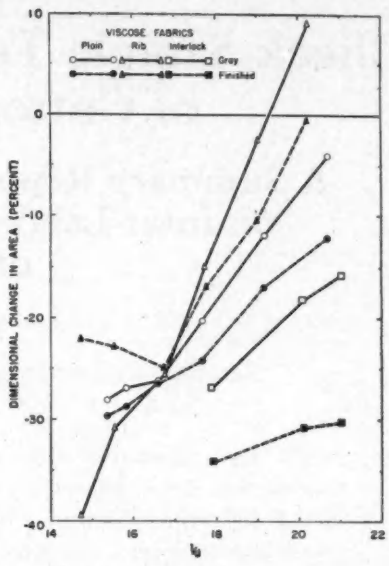

FIG. 7. *The relationship of change in area of viscose fabrics in five launderings to stitch length /diameter of yarn,* l/d, *when the diameter of the yarn equals the experimental value.*

fabrics and for the finished viscose. The shrinkage in area increased with knitting stiffness. Figure 7 shows these results for the viscose fabrics.

On the other hand, the finished acetate-viscose and nylon behaved quite differently. After finishing, the shrinkage in area of these materials usually decreased as the knitting stiffness increased.

Summary

In this study of the geometry of plain, 1 × 1 rib, and interlock knit fabrics made of staple fibers of viscose, acetate-viscose, and nylon, it was found that:

(1) The data for stitch length ranged from $l = 2p + w + 4.18d$ to $l = 2p + w + 6.74d$, as compared with the theoretical value of $l = 2p + w + 5.94d$ which Peirce derived. Weight of the fabrics calculated by Peirce's equation showed good agreement with that obtained by weighing a known area.

(2) The yarn in the finished fabrics neither shrank nor stretched more than 3%. Therefore, the shrinkage or stretching of the yarn contributed little to the dimensional change of the fabric.

(3) The data of wale and course spacings of the laundered gray and finished fabrics followed the parabolic relationship $p^2 = a\,(w + b)$. Those fabrics in which the wale and course spacings before laundering followed a parabolic relationship similar to that of the laundered fabrics exhibited the least change in length and width.

(4) Shrinkage in area of all of the gray fabrics and of the finished viscose fabrics increased with knitting stiffness. Shrinkage in area of the finished acetate-viscose and nylon materials usually decreased as the knitting stiffness increased.

Acknowledgment

Grateful acknowledgment is made to Elinora Dent for laboratory assistance and to Mary A. Fajen for assistance with laboratory determinations and preparation of the data reported in this paper.

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Check Sample Testing of Physical Properties of Cotton with Instruments

A Summary Report Prepared for the Task Group on Inter-Laboratory Check Sample Testing of Cotton Fibers

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The series of interlaboratory check tests of the physical properties of cotton fibers summarized below represents the first large-scale effort to determine the extent to which different laboratories agree or disagree in their measurements of the fiber properties of length, strength, and fineness. In setting up these tests, the laboratories were instructed to use their regular test procedures and no effort was made to achieve uniformity of procedure. No one should, therefore, attempt to read into the report reproducibility of results in terms of equipment or methods. It is expected that the interlaboratory check sample tests will be continued, and that they will ultimately lead to precisely defined methods that should result in a much better agreement between laboratories. The Task Group on Inter-Laboratory Check Sample Testing of Cotton Fibers has approved the publication of a summary of the results of this first series of tests for the information of all laboratories interested in cotton fiber measurements.—Walter M. Scott.†

THE INCREASED USE of instruments by the industry for the measurement of the length, strength, and fineness of cotton has indicated a need for the maintenance of a uniform level of testing within individual laboratories and between different laboratories. In order to ascertain the present uniformity with which results are obtained by use of the Fibrograph, Pressley, and Micronaire instruments in determining these physical properties of cotton, a Task Group was appointed by Committee D-13, Subcommittee A-1-1, Cotton and Its Products, of the American Society for Testing Materials, to conduct a program of interlaboratory check sample testing, with each laboratory following its regular test procedures. The Task Group was authorized to arrange for the preparation and distribution of a series of check samples and to report on the results.

Five cottons were obtained for use for the preparation of check samples. They were of the following varieties: Rowden, Deltapine, Dixie Triumph, Sealand, and Acala 1–23–11–3. Each cotton was blended by the Southern Regional Research Laboratory to provide uniformity within each lot by use of textile mill equipment. In each case the cotton was subjected to opening and picking, carding, and recarding. Conventional speeds, settings, and weights per yard were used. This handling represented a minimum of 576 doublings. The sliver from the second carding operation was packaged in approximately ¼-lb. quantities to give the individual samples for distribution.

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† Chairman, Task Group on Inter-Laboratory Check Sample Testing of Cotton Fibers, Section I, Subcommittee A-1, Committee D-13, American Society for Testing Materials.

TABLE I. SUTER-WEBB ARRAY, WEIGHT FINENESS, MATURITY, AND pH OF TEST SAMPLE COTTONS

Cotton	Upper quartile length (in.)	Mean length (in.)	Coefficient of variation (%)	Weight fineness (μg./in.)	Maturity (NaOH) (%)	pH
Rowden	1.02	0.80	34	5.4	86	6.5
Deltapine	1.23	1.06	26	4.4	83	6.5
Dixie Triumph	1.06	0.86	30	4.6	74	6.8
Sealand	1.46	1.10	40	3.4	72	7.05
Acala 1–23–11–3	1.16	0.98	27	4.4	83	6.3

TABLE II. SUMMARY OF EVALUATION OF 10 RANDOMLY PICKED SAMPLES OF EACH CHECK COTTON

Cotton	Fibrograph U.H.M.* (in.)	Fibrograph Mean (in.)	Fibrograph U.R.† (%)	Pressley index	Micronaire value
Rowden					
High value	0.974	0.762	79.5	7.733	5.42
Low value	0.942	0.740	78.0	7.427	5.20
Range	0.032	0.022	1.5	0.306	0.22
Average	0.952	0.752	79.89	7.554	5.323
Standard deviation	0.010	0.007	0.49	0.109	0.064
Deltapine					
High value	1.165	0.994	85.3	7.342	4.58
Low value	1.149	0.960	83.5	7.158	4.38
Range	0.016	0.034	1.8	0.184	0.20
Average	1.158	0.980	84.62	7.267	4.505
Standard deviation	0.005	0.010	0.57	0.059	0.068
Dixie Triumph					
High value	1.001	0.832	83.3	6.886	4.42
Low value	0.982	0.800	80.8	6.631	4.30
Range	0.019	0.032	2.5	0.255	0.12
Average	0.992	0.813	82.00	6.755	4.360
Standard deviation	0.007	0.010	0.70	0.085	0.038
Sealand					
High value	1.336	1.040	77.9	8.037	3.25
Low value	1.317	1.002	76.0	7.824	3.11
Range	0.019	0.038	1.9	0.213	0.14
Average	1.324	1.019	76.90	7.935	3.170
Standard deviation	0.006	0.011	0.69	0.073	0.045
Acala 1–23–11–3					
High value	1.097	0.926	84.6	6.667	4.60
Low value	1.062	0.886	83.4	6.487	4.47
Range	0.035	0.040	1.2	0.180	0.13
Average	1.081	0.908	83.97	6.571	4.530
Standard deviation	0.011	0.011	0.34	0.085	0.047

* Upper-half mean length.
† Uniformity ratio.

The Suter-Webb array, weight fineness, maturity, and pH of each blended lot of cotton, determined by the Southern Regional Research Laboratory, are shown in Table I. The pH values indicate that the cottons had been picked prior to any serious exposure to wet weather, that very little, if any, field deterioration had occurred, and that they were in good condition.

Ten packages were selected at random from each of the five lots of blended cotton from those prepared for distribution. These were tested by the Southern Regional Research Laboratory for length, strength, and fineness by use of the Fibrograph, Pressley, and Micronaire instruments, respectively. This was done to ascertain the uniformity in test results on samples from each lot as obtained in a single laboratory and

TABLE III. SUMMARY OF INTERLABORATORY CHECK SAMPLE TEST RESULTS

Cotton	Fibrograph U.H.M. (in.)	Fibrograph Mean (in.)	U.R. (%)	Pressley index	Micronaire value
No. of laboratories→	55	55	55	69	55
Rowden					
No. of reports	108	108	108	137	109
Highest value	1.02	0.85	85	8.56	5.90
Lowest value	0.86	0.61	70	6.13	4.67
Range	0.16	0.24	15	2.43	1.23
Average	0.946	0.737	77.8	7.460	5.297
Standard deviation	0.029	0.044	3.3	0.353	0.219
Deltapine					
No. of reports	108	108	108	138	109
Highest value	1.24	1.09	91	8.53	5.20
Lowest value	1.04	0.76	71	6.13	3.80
Range	0.20	0.33	20	2.40	1.40
Average	1.166	0.960	82.2	7.182	4.547
Standard deviation	0.033	0.051	3.4	0.336	0.227
Dixie Triumph					
No. of reports	107	107	107	135	106
Highest value	1.08	0.90	88	7.90	5.10
Lowest value	0.86	0.60	69	5.97	3.67
Range	0.22	0.30	19	1.93	1.43
Average	0.993	0.782	78.6	6.863	4.367
Standard deviation	0.031	0.043	3.1	0.323	0.226
Sealand					
No. of reports	108	108	108	138	109
Highest value	1.43	1.16	94	8.85	4.10
Lowest value	1.03	0.71	58	6.55	2.70
Range	0.40	0.45	36	2.30	1.40
Average	1.301	0.913	70.2	7.900	3.259
Standard deviation	0.056	0.083	5.3	0.377	0.240
Acala 1–23–11–3					
No. of reports	106	106	106	136	108
Highest value	1.16	0.98	88	7.75	5.30
Lowest value	1.02	0.80	74	5.62	4.10
Range	0.14	0.18	14	2.13	1.20
Average	1.091	0.886	81.2	6.746	4.562
Standard deviation	0.029	0.039	2.8	0.342	0.212

to give an idea on the thoroughness of blending. The results are summarized in Table II. Since the standard deviations are well within the tolerances allowable between replicate tests, it is thought that the cottons were very well blended in each instance. The data may be compared with the summary of the interlaboratory check test results given in Table III.

Ten check samples, two of each of the five cottons, were sent one at a time at 2-week intervals to 83 laboratories which previously had indicated a desire to participate in the work. The samples were designated by number, 1 to 10, inclusive. Each laboratory was assigned a code number and was not designated by name in reports of test on individual sample lots of cotton. Reports of tests were received from 78 laboratories. Of this number, 55 had Fibrographs, 69 had Pressley testers, and 55 had Micronaires. Fifty-two were laboratories in textile mills, and of these, 32 had Fibrographs, 46 had Pressley testers, 36 had Micronaires, and 25 had all three instruments.

The results of the interlaboratory check sample testing are summarized in Table III. The summary of results shows about the same ranges and standard deviations for each of the five cottons and indicates that the testing variations on the replicate samples of each cotton were very similar. It is not to be construed that the test results reported by each laboratory on the replicate samples were identical. In some cases they varied widely. The number of laboratories reporting values (average of tests made on a check sample) outside the limits of the mean values

TABLE IV. NUMBER OF LABORATORIES REPORTING AVERAGE VALUES OUTSIDE THE LIMITS OF THE MEAN ±1 STANDARD DEVIATION FOR THE 10 CHECK SAMPLES

Number of times outside	Number of laboratories outside limits				
	U.H.M.	Fibrograph Mean	U.R.	Pressley index	Micronaire value
0	14	10	13	17	17
1	4	9	9	13	8
2	11	7	8	12	11
3	9	7	7	9	4
4	7	10	4	6	3
5	5	2	4	4	5
6	3	5	3	1	2
7	0	1	3	1	1
8	0	1	2	2	2
9	1	1	0	3	1
10	0	1	1	1	1
Total no. of laboratories	54	54	54	69	55
Outside limits 2 or more times	36	35	32	39	30
Outside limits on both high and low sides	9	3	6	8	3

± 1 standard deviation for testing the entire ten check samples is shown in Table IV. In the few cases where a laboratory had not reported results it was considered within the limits. It is apparent that some test practices, calibration of test equipment, or test conditions in a good proportion of the laboratories have biased the results reported by them to be consistently either high or low and outside the standard deviations. In this connection, it can be cited that 20 laboratories reported the use of conditions deviating more than ± 2% in R.H. and/or ± 2°F from the standard atmosphere recommended by the A.S.T.M. of 65% R.H. and 70°F.

Considering that the check sample testing of the physical properties of cotton by use of instruments has been the first attempt on a large scale, the results are encouraging. Wider ranges in values and standard deviations were observed than meet good standards of tolerance. Such variations can be reduced by stricter attention to the application of techniques recommended for use of the individual instruments, maintenance and calibration of test instruments and auxiliary instruments such as balances, and conditioning of samples.

It was observed generally that laboratories having an average high or low level of test consistently reported high or low values correspondingly for all the individual check samples. A few exceptions were noted. The results clearly indicate the need for standardization of procedures and instruments to equalize the level of testing among laboratories and in the individual laboratories. Much can be done toward accomplishing this through a continuing program of check sample testing.

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The Supercontraction of Keratin

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Introduction

By appropriate mechanical and chemical treatment, keratin fibers can be made to contract by about 30% of their original length. Astbury and Woods [2] introduced the term "supercontraction" to describe this phenomenon, since in their earlier work the contraction usually appeared as a recovery (following stretching) to a length shorter than the original. Much work concerning supercontraction has been chemical in nature [5, 12], and it has been established that changes, such as the destruction of the cystine bridges between the polypeptide chains of the keratin or a reduction in the degree of hydrogen-bonding or of salt linkage, facilitate supercontraction.

Following the work of Astbury and Woods [2], it was widely accepted that the contraction in length of the fiber is direct evidence of a contraction in length by further folding of the molecular chains of the protein. The literature records several proposed structures for the contracted molecule. The phenomenon acquired a broader significance when Astbury suggested a close similarity between supercontraction of hair and muscular contraction [1].

The molecular-folding hypothesis gains support from the mass of related phenomena among synthetic and natural polymers in which changes in shape are determined by molecular configurations. But whereas the recovery in shape of a length of rubber may be shown to be directly related to molecular configurations, it does not follow that dimensional changes in a natural fiber having a histological and fine histological structure are as simply related to molecular events. Seeking evidence of configurational changes, Astbury and Woods [2] and Whewell and Woods [13] examined supercontracted fibers by means of x-rays, and noted the occurrence of disorientation and the recrystallization of the protein in the β-configuration. The appearance of the β-form, which is characteristic of stretched hair and grossly denatured proteins—*i.e.*, of straight rather than folded chains—was thought to result from changes subsequent to the initial contraction. On the whole, the x-ray work failed to provide evidence of the type of molecular change causing supercontraction, and this failure remains a major obstacle to the understanding of the phenomenon.

The possibility that the change in length of the whole fiber may be more directly related to changes at the histological level has been considered by Woods [14], who showed that the fibrous cells constituting the cortex of the keratin fibers closely parallel the whole fiber in their length changes during supercontraction, thus proving that the length change must be associated with a structural feature smaller than the whole cell. The present author has made similar observations, and, further, by observing the movements of strings of pigment granules within the cells, has concluded that the intracellular fibrils, which constitute the bulk of the cell, also shorten to the same degree and do not merely crumple or disorient during contraction [8]. The intracellular fibrils (macrofibrils) themselves are in turn composed of still finer fibrils [7, 10, 15], which may be referred to as "microfibrils," and it is possible that these may play some special role in supercontraction. The size of the macrofibrils is such that they may be examined conveniently in the electron microscope. The object of this paper is to describe electron microscopic observations which suggest that a twisting of the macrofibrils occurs during the supercontraction of the whole fiber.

Experimental

The most obvious approach to the problem of the state of the intracellular fibrils in supercontracted fibers might seem to be the isolation and examination of fibrils from supercontracted fibers. This method could not be used, however, because the various methods of reducing fibers to a fine enough state for electron microscopy proved unsatisfactory when tried with supercontracted material. Mechanical grinding

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produced only particulate forms lacking a fibrous structure. This observation is in accord with other observations (x-ray, polarization optics, elasticity, etc.), which all indicate an impairment of the fibrous texture. Enzymic digestion, the most suitable method of reducing hair to a fine fibrillar state, failed also, because with all forms of contracted fibers the fibrous cortex was rapidly and preferentially removed, leaving only a hollow resistant tube or tubular fragments derived from the outer layers of the cuticle [9].

Woods earlier met this same difficulty, and solved it by causing cortical cells themselves to contract after their release from fibers which had been pretreated to dispose them towards contraction [14]. In effect, this technique was followed here. A wool in which the disulfide cross-linkages between the polypeptide chains had been reduced and then prevented from reclosing by the ethylation of the thiol groups was used for the experiments.

$$W\text{—S—S—}W \longrightarrow W\text{—SH} \longrightarrow W\text{—S } C_2 H_5$$

The ethylated wool was digested by pepsin, and could then be broken down easily into a fine fibrillar form by mild procedures for study of the fine structure. Such wool is also readily disposed to supercontract, as shown by the experiments of Brown, Pendergrass, and Harris [3] and those of Speakman [12] carried out on similar material. When fibrillar fragments of this reduced wool were examined, the macrofibrils appeared to be twisted, in contrast to the straight appearance of macrofibrils from normal wool digested with trypsin or disintegrated by steeping in ammonia. It seemed probable, therefore, that the twisting was associated with supercontraction.

Preparation of Supercontracted Wool Fibrils

Fine merino wool was chopped into short lengths and cleaned by treatment in a Soxhlet extractor with petroleum ether followed by washing in warm water containing a trace of a neutral detergent. The purified wool was simultaneously reduced and ethylated by the method of Brown, Pendergrass, and Harris [3]. 500 ml. of a solution containing 5% sodium bisulfite was brought to neutrality by the addition of solid sodium bicarbonate, 2 g. of wool and 2 ml. of ethyl bromide were added, and the whole was sealed in a flask and maintained at 40°C for 36 hrs. The ethylated wool was washed thoroughly, added to a pepsin solution (1000 ml., 0.05%, pH 1–2), and digested for several days until sufficient disintegration had occurred [11].

During the prolonged digestion of the ethylated fibers at 40°C in solutions of pH 1–2, many of the released cortical cells were observed to have contracted in length. The twisted appearance of the fibrils would also indicate contraction, although actual length measurements cannot be made of these.

When sufficient disintegration of the fibers had occurred, the remaining wool was mechanically disrupted and homogenized with water in a Waring Blendor. A fine suspension of fibrils for electron microscopy was separated by fractional centrifugation.

Electron Microscopy

The microscope used was a R.C.A. Type EMU; standard methods of mounting and shadowing were used.

The twisting of the fibrils was apparent in both shadowed and unshadowed fields. Various other appearances of the fibrils could be referred back to the twisted forms, such as the opened-out forms visible in portions of Figure 1.

Discussion

These observations suggest that twisting of macrofibrils occurs during some kinds of supercontraction, although other changes may also contribute to the total shortening. The angle of twist approaches a maximum of 45°, and this would be sufficient to account for the greater part of the total shortening (30% of original length). Such twisting would also account for the dispersion of the x-ray photographs and the fall in birefringence which occurs. The chemical data can be fitted in with the hypothesis. The report of Whewell and Woods [13] that they observed a 20% contraction without great derangement of the x-ray pattern is in apparent disagreement and requires further consideration.

The possibility that the contraction of isolated fragments might differ from that of the whole fiber needs to be considered, but there does not seem to be any strong reason to expect a difference. One would expect rather that the behavior of fragments uncomplicated by the confining effects of adjacent material and higher histological structures (cells and cuticle) would follow more faithfully the contractions of their component parts.

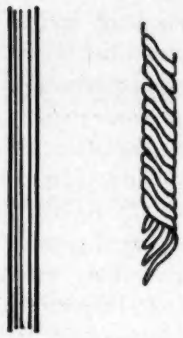

FIG 2. *Schematic diagram, showing:* left—*parallel alignment of microfibrils in untreated wool; and* right—*spiral arrangement of microfibrils in a twisted macrofibril.*

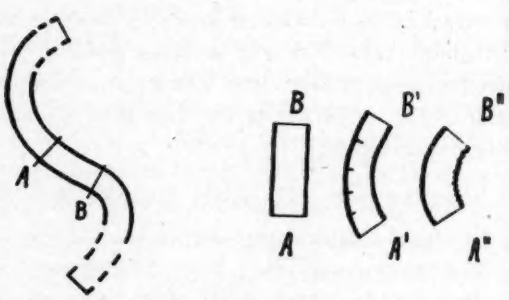

FIG. 3. *Segment of microfibril, showing results of differential expansion and contraction of its opposite sides.*

Considering the twisting in a purely geometrical way, it is readily seen that it could be produced by a bending of the component microfibrils, which, as shown in Figures 2 and 3, would throw these into arcs or helixes. Such bending could result from either a contraction (Figure 3, *A" B"*) or an extension (*A' B'*) of one side of the microfibrils. For instance, an extension of the outer exposed surfaces of the microfibrils might well follow a preferential chemical attack on these surfaces, leading to greater swelling. On the other hand, a contraction of the inner face could conceivably follow a more readily induced molecular folding on that face. A further possibility is that each of the individual molecules composing a microfibril assumes a bent form. Since the geometrical consequences of these possibilities are similar, a study of the micrographs is not sufficient to decide what really happens. In any case, however, it is clear

FIG. 1. *Electron micrograph of fragments of the cortical cells of reduced and ethylated wool, showing twisting of the macrofibrils.* (*Magnification, 7900* ×.)

that the percentage contraction in length of whole fibers cannot be linked directly to a hypothetical change in the length of the molecular chains. On the assumption that each element of the fiber down to the component molecules undergoes the same percentage contraction, it is difficult to account for the actual appearance of the contracted fibrils.

A similarity between muscular contraction and supercontraction has been assumed [1]. If it is accepted that a twisting of the macrofibrils actually occurs during the supercontraction of keratin, little likeness between the two phenomena can be shown. The structural feature of vertebrate striated muscle that is analogous to the macrofibril in dimensions is the myofibril, and these are known to contract in length without twisting by reason of the contraction of their component myofilaments, which remain straight and parallel to the fiber axis in the contracted form [4, 6].

Summary

The examination of fragments of supercontracted wool in the electron microscope enables further insight into the nature of one kind of supercontraction. The macrofibrils in the supercontracted form appear to be twisted, and it is suggested that such twisting rather than molecular folding is directly related to the length changes of the whole fiber.

The twisting of macrofibrils could be due to a bending of the component microfibrils into arcs or helixes. This change could have a molecular basis.

Little similarity between contracted muscle and supercontracted keratin can be found by using the electron microscope.

Acknowledgments

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INDUSTRIAL SECTION

Some Properties of Thermoplastic Fiber-Bonded Fabrics*

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Abstract

Test procedures and physical properties are given for cotton, nylon garnett, asbestos, and glass fiber thermoplastic fiber-bonded fabrics. A range of thicknesses for each blend and weight is used to demonstrate a wide variety of fibrous constructions. The tensile strength, air permeability, and water absorption characteristics of four fiber-bonded fabrics are discussed. It is indicated that any textile fiber can be fabricated by this process.

Introduction

The relatively new field of bonded fabrics is rapidly gaining importance in the textile world. The proper use of these materials promises to establish a permanent position for them in many varied applications, including mechanical and industrial uses.

The term "bonded fabrics" occurs frequently in newspapers and textile magazines, but there is almost no literature available which gives the manufacturing details or the range of physical and chemical properties for a given bonded fabric.

As a step toward customer acceptance, the potential users of bonded fabrics should know and understand in detail how bonded fabrics are constructed. Only when this is done will they be able to use the materials available today intelligently and with assurance.

The process utilizing thermoplastic binder fibers for fabrication was developed in 1937, shortly after the synthetic fiber vinyon was made available commercially. There are a number of patents covering the use of binder and non-binder fibers as well as end-use and process patents [4, 5, 6, 7]. Some of the initial fabrics produced were developed for filtration of milk and also for a tea-bag fabric. They are still in current use and are but forerunners of the many different varieties of material which have followed.

Actually, the bonded fabric field is, to a great extent, unexplored. Consider (1) the variables which exist—for example, the many fibers, with their various diameters, crimp, and staple lengths; (2) the bonding materials, with their inherent characteristics; and (3) a combination of the first two factors, resulting in a variety of combinations. It is understandable that the infinite number of combinations possible correspondingly increase the range of possible applications.

The flexibility of the fiber-bonded process makes possible a range of products previously not made available by any other method. This is due to the manufacturing variables in which bonding temperature and pressure, amount of binder fiber used, and selection of non-binder fiber can be controlled.

As improved synthetic fibers and bonding resins are developed, improved bonded fabrics will automatically become possible. In this regard, it will be

* The material reported in this paper was presented at a meeting of The Electrochemical Society, Inc., at the Benjamin Franklin Hotel in Philadelphia, Pa., May 7, 1952.

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TABLE I. FIBER BLENDS STUDIED

Blend No.	Percent	Fiber
I	20	Vinyon, 3 denier
	80	Cotton shoddy
II	20	Vinyon, 3 denier
	80	Nylon garnett, 15 denier, heavy crimp
III	25	Vinyon, 3 denier
	25	Nylon, 6 denier
	50	Asbestos, 3R Canadian Chrysotile
IV	20	Vinyon, 3 denier
	80	Fiberglas G fiber, 2 in. staple length, 204 filaments per yarn

TABLE II. OTHER NON-BINDER FIBERS

Fiber	Description
Synthetic	
Nylon	Denier 1.5, 3.0, 6.0, 15.0, garnett
Dynel	Denier 3.0, 24.0, garnett
Saran	Denier 10, 30
Acrilan	Denier 3.0, 5.0
Dacron	Denier 3.0
Orlon	Denier 3.0
Viscose	Denier 1.5, 3.0, 5.5, 15, garnett
Acetate	Denier 3.0, garnett
Celcos	Denier 17.0
Vicara	Denier 3.0
Caslen	Denier 145
Alginate	Denier 3.0
Natural	
Wool	Virgin, reused, waste, shoddy
Silk	Raw
Flax	Natural, bleached
Jute	Waste

seen that the process under discussion can easily be used to prepare a fibrous structure for even the newest fiber.

The purpose of this paper is to present and discuss the physical properties of four characteristic thermoplastic fiber-bonded fabrics. The test data for these representative samples show a wide range of physical and chemical properties in various fibrous constructions, and explain, to a certain degree, why fiber-bonded materials should have expanding uses.

Experimental Procedure

Materials

Four fiber blends were investigated in the present study. The fibers chosen for test have a favorable potential for industrial applications. They represent a re-used natural fiber, a re-used synthetic fiber, and two mineral fiber blends. The test samples were free from sizing or other chemical binders. The composition of these blends is given in Table I.

In addition to the fiber blends presented here, satisfactory samples have also been prepared from the fibers listed in Table II.

Preparation of Bonded Fabrics

The first step in the preparation of bonded fabrics is the blending together of thermoplastic binder fibers with non-binder fiber blends. The mixture is then carded. If the unpressed batt is formed by straight carding, the fibers tend to be aligned in the direction of carding. This construction will also be evident in the final and pressed product and will show a greater tensile strength in the lengthwise direction than in the widthwise direction. However, batts prepared by crosser-carding or by air blowing methods develop the desirable property of having approximately equal strength in both directions. After carding, the batt is hot-pressed, causing the thermoplastic fibers to fuse and bond the entire fibrous mass.

This process differs radically from the method used for producing the bonded fabrics which are formed by the impregnation of fibrous batts with dispersions, emulsions, or solutions of sizing or other bonding substances.

The fiber mixtures described in Table I were blended; weights were adjusted; and the blends were straight-carded on a Davis & Furber laboratory card.

From each batt, individual samples, 6 in. × 6 in., weighing 6.0 oz./sq. yd. and 18.0 oz./sq. yd., were taken and pressed for 1 min. at 300°F on a Carver laboratory press (6 in. × 6 in. platen size) to the indicated density. For test purposes, the maximum pressure for each sample was limited to 284 p.s.i.

Physical Properties Investigated and Test Methods

The fiber blend, thickness, and weight of the product must be predetermined to comply with end-use requirements. By varying the thickness, for example, a single blend and weight will give products ranging in appearance and properties from a semi-rigid batt construction to a felt-like material to a paper-like product.

Thickness was determined by the A.S.T.M. method (designation D 461–51–8) [1], except for the lofty samples which exhibit less than the density of 20% specific gravity. These were measured with-

out the 10-oz. presser foot weight. This is conventional procedure for soft material. A unique property of a thermoplastic fiber-bonded fabric is that the fibrous structure tends to retain the fabric thickness at which the heat and pressure are applied. By controlling the thickness during activation, a wide range of physical properties for a given fiber blend and weight is made possible.

Density is expressed as percent specific gravity, and is determined as follows:

$$\text{density} = \frac{\text{weight (oz./sq. yd.)}}{\text{thickness (in.)}} \times 0.1335.$$

It has been found that the density can be used to identify and predict the general nature of any fiber blend. Different fibrous structures of identical density exhibit similar physical properties, such as flexibility, strength, permeability, and porosity. All of the test data presented herein is shown with reference to the fabric density.

Air permeability was determined by the A.S.T.M. procedure (designation D 461-51-S5) [2], expressed in c.f.m./sq. ft./0.5 in. H_2O. Air permeability values presented herein can be correlated with the permeability values of water or other liquids.

Tensile strength was determined for lengthwise direction by the A.S.T.M. procedure (designation D 461-51-11) [3] for wool felt, using a Scott Testing Machine. Tensile strength is an important consideration for use as design data.

Water absorption was determined as follows. A 2 in. × 2 in. sample was weighed. The sample was then immersed in water, with wetting agent added (necessary to wet very dense construction). The excess water was drained, and the water-saturated sample was weighed. The increase in weight was recorded as the percent water absorption. Water absorption values can be correlated with the absorption values of other liquids.

Other values for a given blend, not reported here, which vary with the density are: Mullens bursting strength, scuff-resistance, Shore A Durometer hardness, and water permeability.

Results

Effect of Fiber Blend on the Physical Properties of Fiber-Bonded Fabrics

All of the samples were prepared under identical carding and bonding conditions. As a result, the variations in test data for equivalent weight in each case reflect bonding and permeability properties of the blends used. Figures 1–8 present the results obtained.

Tensile strength.—The tensile strengths of all blends up to a density of 15%–20% correspond fairly well. This can be explained by the cohesive and adhesive bonding action of the thermoplastic fiber. Up to the 15%–20% density range, the vinyon binder fiber holds the fibrous mass together by cohesive forces—that is, the only bonding action occurs between crossing or adjacent vinyon fibers. Above that density, adhesive forces begin to develop between the binder fiber (vinyon) and the nonbinder fiber.

The tensile strength values developed by these bonded fabrics above the 15%–20% density range vary with the vinyon bonding properties of the individual fibers. All of the factors controlling this bonding mechanism are not understood. However, the fiber surface, whether it is absorbent, irregular, smooth, or compatible with vinyon, would appear to be pertinent.

It has been shown by other tests that fiber diameter is another factor which controls the tensile strength developed. For samples having the same weight, density, and percent binder fiber, 3.0-denier viscose rayon was found to develop twice the tensile strength of 5.5-denier viscose rayon and four times the tensile strength of 15.0-denier viscose rayon. The finer denier presents increased fiber surface area per unit weight, permitting improved bonding of the fibrous structure.

In general, the higher densities develop higher tensile strength. The maximum density values (indicated in Figures 1–8) were obtained under identical bonding conditions (284 p.s.i., 300°F, for 1 min.). Therefore, the variations of the maximum densities obtained are indications or results of the tendency of the fiber blend to compress. In general, fiber diameter and crimp control the tendency of the blend to compress (see Table III).

The relatively high tensile strength values obtained with cotton and asbestos can be explained by noting that these fibers have a tendency to compress and have irregular fiber surface as well as fine fiber diameter.

The low tensile strength of the glass fiber sample is probably due to its poor affinity for bonding to vinyon.

TABLE III. DEGREE OF COMPRESSION OF TEST BLENDS

Order of compression*	Blend No.	Predominant fiber	Comments
1	III	Asbestos	Very fine fiber diameter; fiber tends to matt under light pressure
2	I	Cotton	Same as above, but larger fiber diameter
3	IV	Fiberglas	Very fine fiber diameter; round and noncompressible fiber occurring in large numbers in the yarns
4	II	Nylon garnett	Relatively coarse fiber; heavy crimp; round and resilient fiber

* 1—most compressible; 4—loftiest.

The low tensile strength of the nylon garnett sample would appear to be a result of its resistance to compression. Very likely, high values can be obtained by increased bonding.

It must be mentioned that the maximum tensile strength values presented here are not the limiting values for a particular fiber blend. The tensile strength or density of a blend can be increased by using more binder fiber, greater bonding pressure, higher bonding temperature, or heavier fabric weight.

Water absorption.—As a general rule, the saturated water absorption value is an indication of the volume of voids present in a fibrous structure. However, in low-density structures, this rule is limited by the amount of water that can be held by capillary action. There may be variations caused by the individual fiber water absorption values. In general, it is assumed that the water absorption value corresponds to the porosity of the fibrous structure.

Air permeability.—The differences in air permeability values of the various blends for similar weights and densities are caused by the differences in effective fiber diameters (see Table IV).

Use of blends.—In some cases, the physical properties of a single fiber blend can be improved for a given end-use by admixture of different fibers. For example, in filtration applications fine fibers are used for quality filtration; coarse fibers are used in the same blend to reduce the pressure drop. A change in fiber blend can be used to develop minute changes in the final product.

TABLE IV. RELATIVE PERMEABILITY OF TEST BLENDS

Order of air permeability*	Blend No.	Predominant fiber	Effective fiber diameter (μ)
1	III	Nylon garnett, 15 denier	40
2	IV	Fiberglas, 9.2 μ filament diameter, 204 filaments/yarn	35 (estimated)
3	I	Cotton	10
4	II	Asbestos	less than 1

* 1—highest permeability, etc.

Effect of Weight of Blend on the Physical Properties of Fiber-Bonded Fabrics

Data on the physical properties of blends I–IV are compared for two weights in Figures 1 and 2, Figures 3 and 4, Figures 5 and 6, and Figures 7 and 8, respectively.

Thickness.—For the same density, the 18 oz./sq. yd. samples have three times the thickness of the 6 oz./sq. yd. samples.

Tensile strength of the 6 and 18 oz./sq. yd. samples remains essentially constant for the same blend and density.

Water absorption for the 6 and 18 oz./sq. yd. samples remains essentially constant for the same blend and density.

Air permeability values for the 18 oz./sq. yd. samples of equivalent blend and density are lower than those for the 6 oz./sq. yd. samples due to the increased air-resistance for a given air flow rate caused by three times the number of fibers present per unit area.

For a single blend and weight, the air permeability decreases as the density increases. The highest air permeability values occur at the lowest density which is characteristic of the unpressed batt. The lowest air permeability values tend to level off at the high density values where maximum fiber compression occurs.

Since the air permeability values for the 6 and 18 oz./sq. yd. samples overlap, it is possible to prepare both weights with equivalent air permeability values. For example, the air permeability value for the 6 oz./sq. yd. sample of blend I at density 22% is 20 c.f.m./sq. ft./0.5 in. H_2O; the 18 oz./sq. yd. sample of blend I at density 10% also has an air permeability value

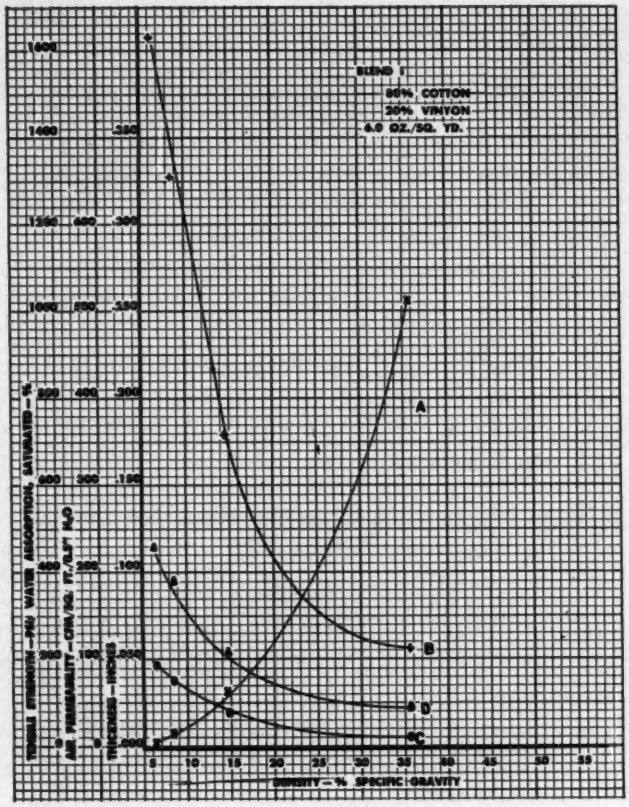

FIG. 1

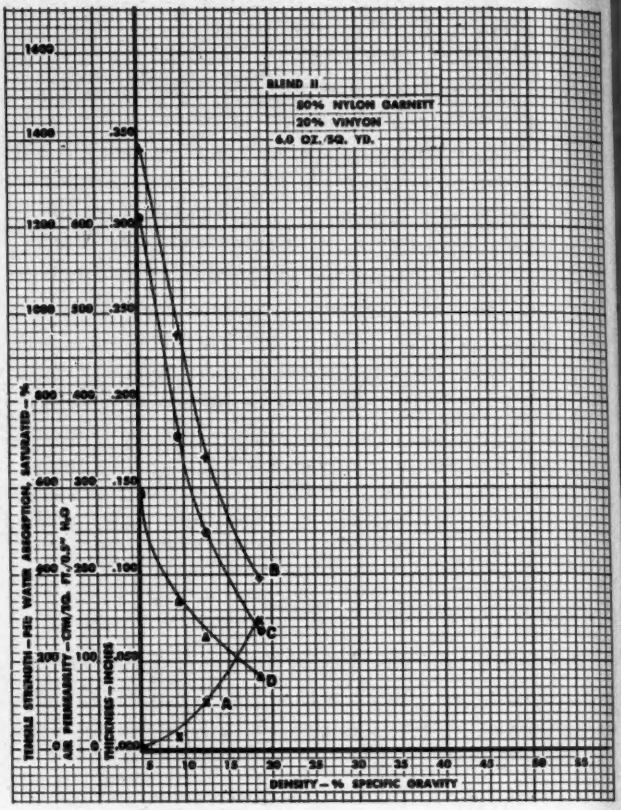

FIG. 3

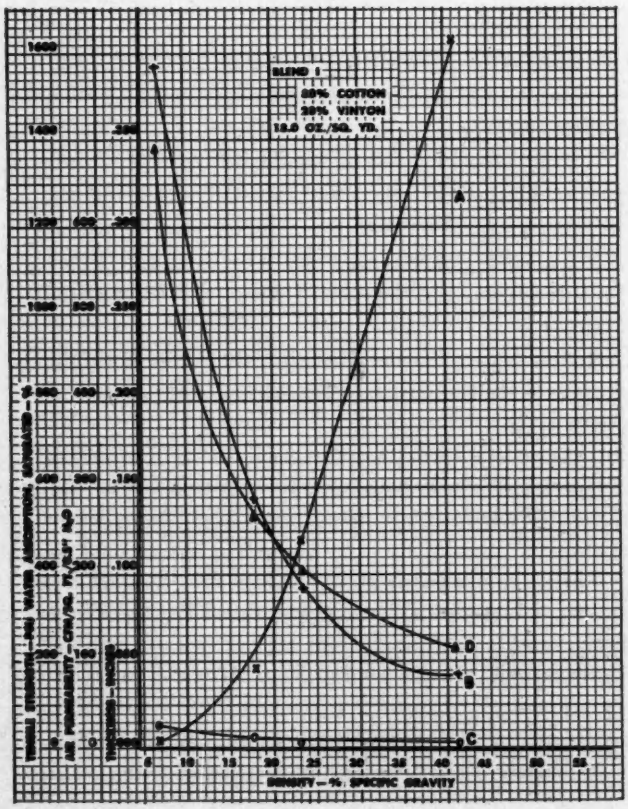

FIG. 2

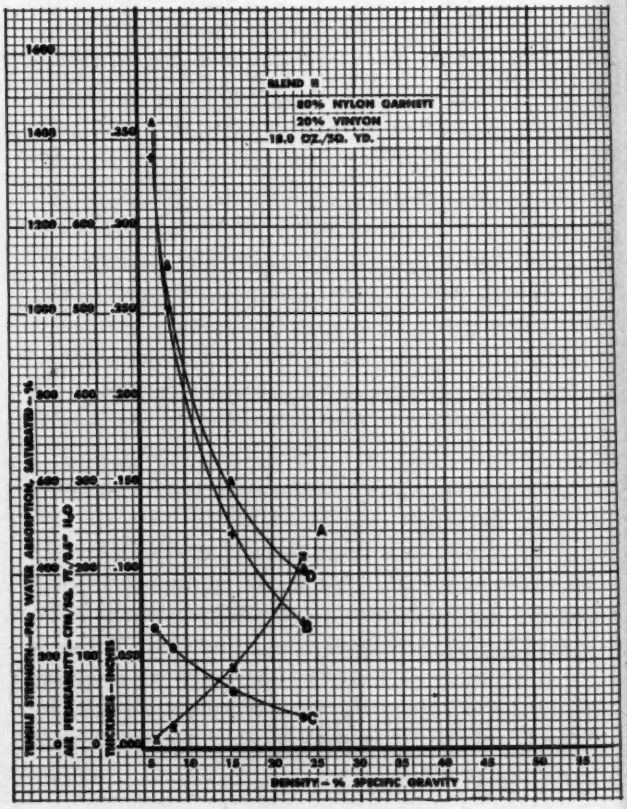

FIG. 4

The curves for the different physical properties are as follows: A—*tensile strength* (×); B—*water absorption* (+); C—*air permeability* (○); D—*thickness* (▲).

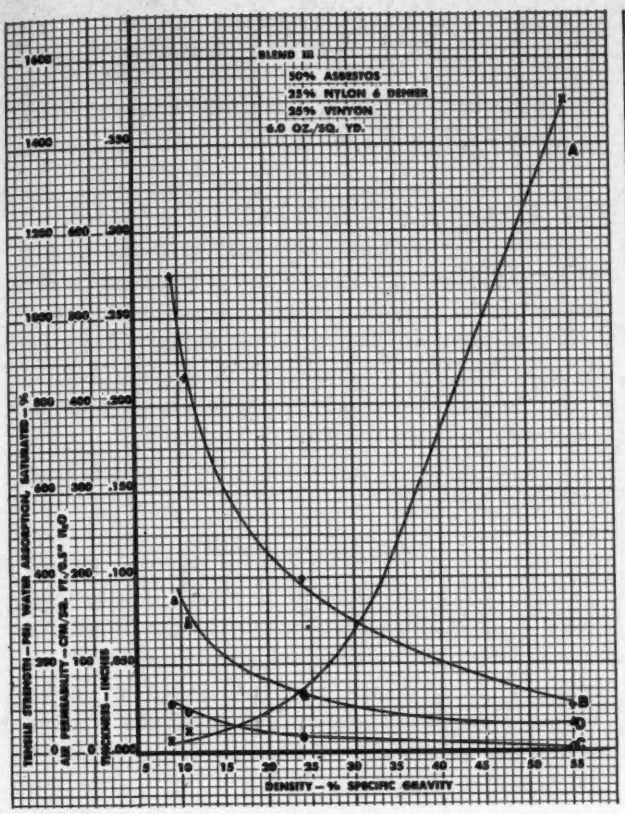

FIG. 5

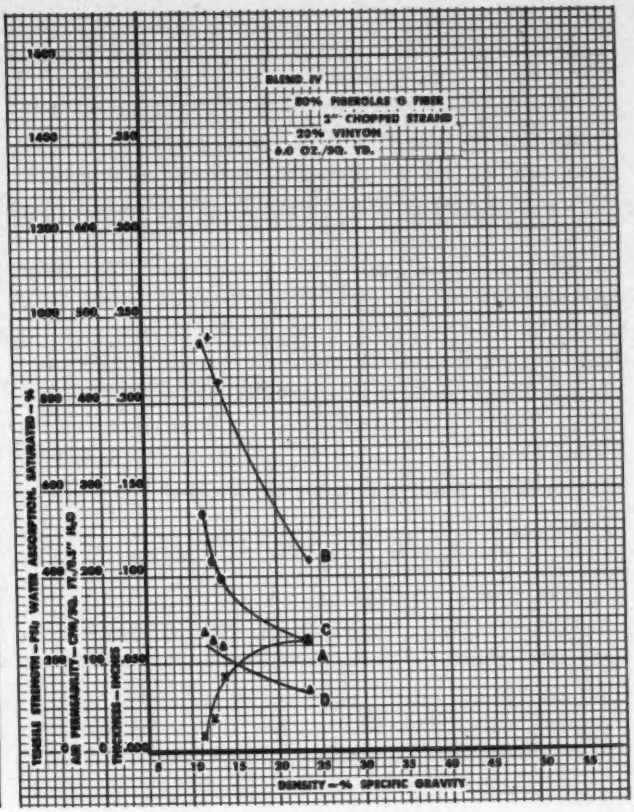

FIG. 7

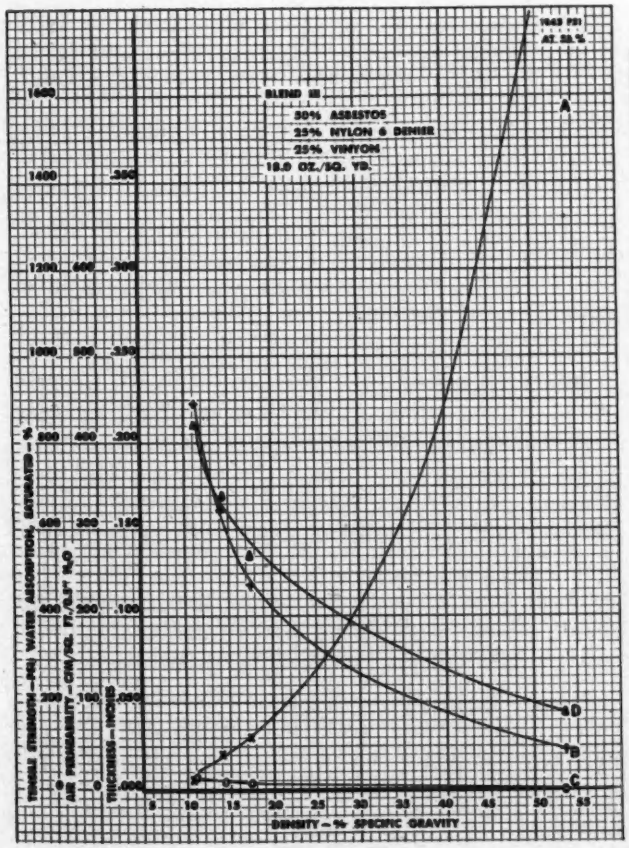

FIG. 6

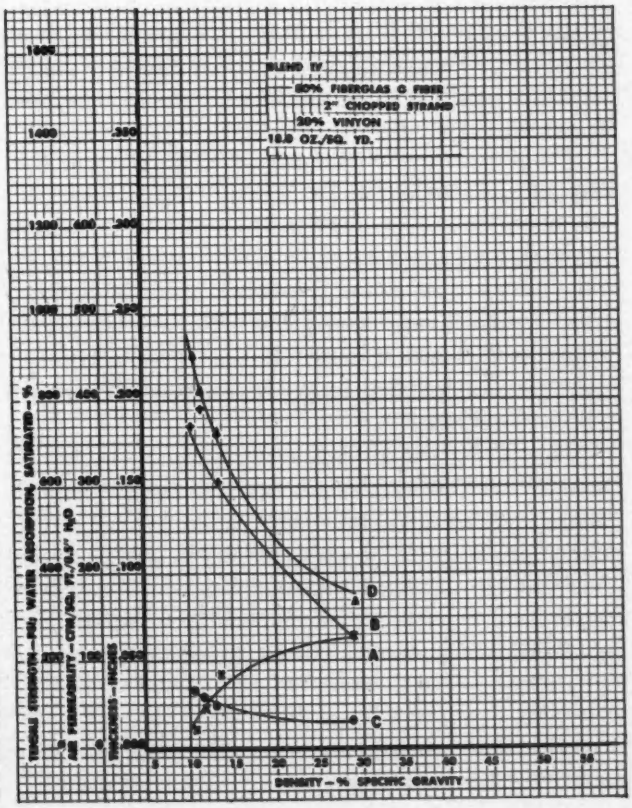

FIG. 8

of 20 c.f.m./sq. ft./0.5 in. H_2O. This type of flexibility, which permits weight variation for a given air permeability, should prove to be useful as a laboratory tool and in the preparation of gas or liquid filter media.

Density.—The high density values in each case were obtained using identical bonding conditions (284 p.s.i., 300°F, for 1 min.). By examination, it can be seen that all of the 18 oz./sq. yd. samples developed higher densities than the 6 oz./sq. yd. samples. Further study will show an increasing density value for an increasing fabric weight when the blends are bonded under identical conditions.

Application of Bonded Fabrics

The tensile strength and scuff-resistance values for bonded fabrics are especially critical values compared to those for woven cloth. In determining or designing bonded fabrics for given applications, these characteristics should be given detailed consideration. A complete analysis of a given end-use should precede the design or selection of a bonded fabric. For example, the required strength, absorption, permeability, scuff-resistance, and chemical stability should be determined. If all of the required values are found to fall within the bonded fabric available range of values, it is quite likely that a bonded fabric can be used which will furnish all of the physical or chemical properties required at a lower cost than that of standard fabrics.

The process discussed herein has the following advantages: it is suitable for the utilization of all textile fibers; it is suitable to meet strict quality-control specifications; delicate manufacturing control will reproduce any of a wide range of physical properties; manufacturing cost is low; manufacturing and delivery time are reduced; it is a flexible type of process, ideally suited to the manufacture of various fibrous structures.

Considering the aforementioned, some mechanical uses for which these bonded fabrics can be designed follow: gas and liquid filtration, wicking, reinforcing fibers for laminated or molded plastics, base cloth for impregnated fabrics, electrical insulation, electrolyte absorbent, battery separators, clothing linings for cold-weather garments, fabrics to withstand corrosive materials, or any of the above where chemical or biological stability is required.

Conclusions

1. The thermoplastic fiber-bonded fabric process permits the production of a material having a very wide range of physical properties from a single blend.
2. The physical properties of bonded fabrics can be controlled by the selection of component fibers.
3. The physical properties of a given blend are controlled by fabric density.
4. It is indicated that any fibers can be fabricated by this process.

Acknowledgment

Grateful acknowledgment is given to Mr. Hugo Boeddinghaus, Vice-President in charge of Production and Director of Research, American Felt Company, for his guidance and encouragement in this work. Since he pioneered and developed a manufacturing process for the foregoing type of fabric, his collaboration has been invaluable.

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(Manuscript received March 12, 1952.)

Some of the Factors Influencing Yarn Tension in Warping*

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Abstract

The successful warping of coned yarn depends to a major degree on applying equal and constant tension on each end of yarn so that smooth homogeneous beams are produced. This paper reports a study made to determine the factors which influence warping tensions. Several variables inherent in the yarn or in a coned yarn package which affect withdrawal tensions have been found. The variables of yarn twist, ballooning of the yarn during withdrawal, yarn speed, and cone size are discussed as factors which control withdrawal tension in warping. The magnitude and frequency of tension variations caused by these factors are shown by graphic records obtained by suitable recording instruments. The three basic methods for applying tension to the yarn have been classified as multiplying, additive, and compensating. The limitations and advantages of tension devices incorporating these basic methods in pure and combined forms are discussed with reference to the basic equations and graphic records.

Introduction

In the manufacturing and processing of textile materials there are many points at which it is necessary to control the tension. The method of controlling the tension and the precision with which it must be controlled vary from process to process. There is perhaps no phase of the textile industry which requires more precise control than that concerned with the processing of synthetic yarns. In the processing of acetate yarn, for example, small variations in tension may be extremely objectionable because the high degree of uniformity of the individual strands exaggerates any slight deviation from the normal arrangement of the fibers in a fabric.

In the manufacture of acetate yarn it is very important that the tension be controlled in the spinning process, in twisting, and in winding. However, of all the processes encountered, the tension in warping is, perhaps, the most critical. In the preparation of section beams, for example, there may be from 600 to 1,000 ends running parallel, each end having a different bobbin or cone as its source. This process is illustrated in Figure 1.

Any variation in the average tension will affect the density of the beam. If the tension from a set of bobbins should increase progressively as the yarn is withdrawn, the first beam wound from the creeling would have a lower density and a greater diameter than the later beams wound from the same creeling. Since the yarn from these beams may eventually be combined in the same fabric, there is a possibility that this variation would be detrimental to the quality of the finished product.

If the tension should vary from end to end in the warp sheet, there would be a variation in density within the beam which would show up as ridges and valleys on the surface of the beam. Obviously, when this yarn is withdrawn from the beam to be woven, some of the ends will be tighter in the fabric since fewer yards of yarn will have been wound in the valleys than on the ridges. This condition, if of sufficiently great magnitude, may cause stretching of the tight ends, and under any circumstances it may cause warp streaks. Therefore, it is very important to control the warping tension when processing acetate yarn. This is true whether the warping is carried out by the yarn producer or by the weaver.

Recognizing the importance of this problem, a considerable part of our development program has been devoted to the study of various types of tension devices commonly used in warping acetate yarn. Tension devices have been classified into a few funda-

* Presented at a meeting of The Fiber Society, Clemson, South Carolina, April 17, 1952.

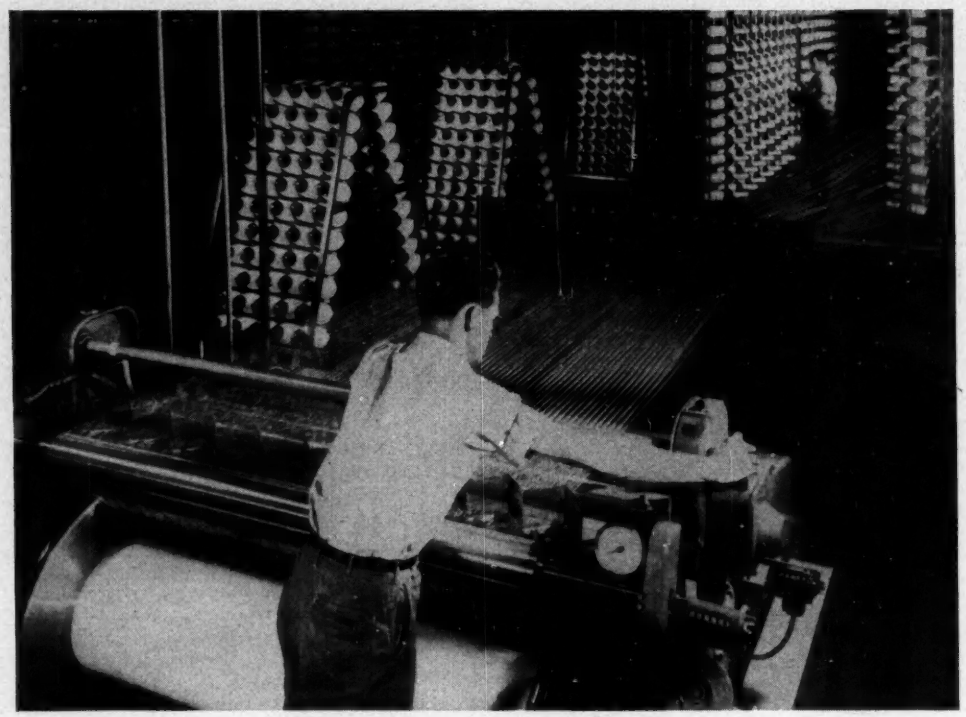


FIG. 1. *Preparation of section beams.*

mental types which illustrate the various principles involved in applying tension to textile materials. It is the purpose of this paper to describe some of the work which has been done in this connection and to establish the relative merits of the various types of tension devices studied.

Description of Apparatus

In carrying out this work, a strain gage tensiometer very similar to the one described at an earlier meeting of The Fiber Society * was used. The instrument as set up in our laboratory consists of a Statham G7 strain gage and the Statham CB7 control unit, as illustrated in Figure 2. This equipment is available commercially and is readily adaptable to the study of tension. The G7 strain gage has a load measuring capacity of 3.5 oz. and is sensitive to frequency variations up to 525 cycles/sec. Its natural frequency is 108 cycles/sec. when equipped with standard tension pulleys as shown in Figure 2. The advantage of using this type of equipment is obvious since it is a convenient means for transferring force into electrical energy which may be recorded with commercially available equipment. This makes it possible not only to obtain an accurate record of the tensions being studied, but also to establish the relationship of cause and effect by means of the time scale. Another advantage of the strain gage instrument is the

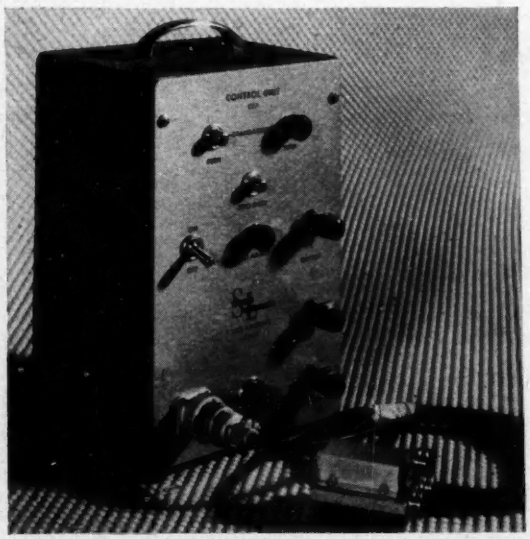


FIG. 2. *Strain gage tensiometer.*

* Nistico, F., Sprague, B. S., and Work, R. W., A High-Speed Recording Yarn Tensiometer, TEXTILE RESEARCH JOURNAL 22, 99–110 (Feb. 1952).

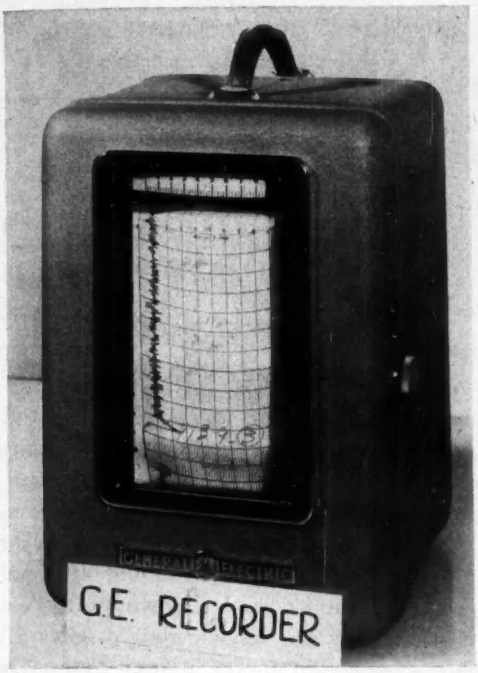


FIG. 3. *G.E. photoelectric recording microammeter.*

extremely low inertia which permits the recording of high-frequency variations in tension which cannot be evaluated with a conventional hand-type tensiometer.

For recording long-range variation in tension the G.E. photoelectric recording microammeter was used; this instrument has a 75-microampere movement with a 4-sec. response and chart speeds of ½ in./min. and ½ in./hr. This recorder is shown in Figure 3. By using this instrument, it is possible to obtain the low-frequency variation in tension over long periods of time. Thus, the changes in average tension encountered throughout a process cycle may be recorded. This instrument has a further advantage of damping out the high-frequency components which might complicate the interpretation of data. This instrument was found to be reasonably stable and sufficiently accurate and sensitive for the purpose of studying long-term tension variations.

For recording high-frequency variations the Brush Model BL201 magnetic oscillograph was used in combination with the Brush Model BL913 D.C. amplifier, as shown in Figure 4. This instrument has a frequency response of 0 to 100 cycles/sec., which closely matches the range of the strain gage. This instrument is subject to zero drift, as are all D.C amplifiers,

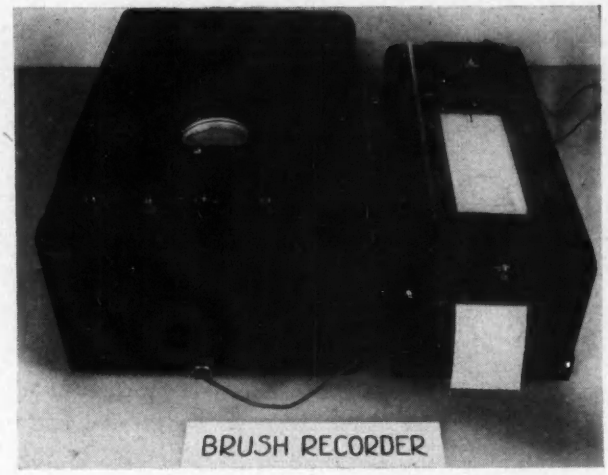


FIG. 4. *Brush magnetic oscillograph and amplifier.*

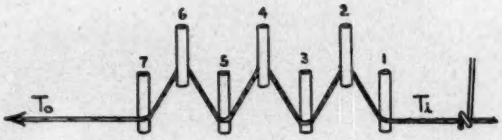
but it was found to be sufficiently stable for any short-range recording which was required.

Classification of Tension Devices

Although the information which can be obtained with this equipment is helpful per se, it must be carefully interpreted if its maximum value is to be realized. In order to explain the manner in which tension is applied to yarn by the many forms of warp tensions, it was found desirable to derive the mathematical equations of the basic yarn tensioning methods. Once this basic knowledge is available, it then becomes possible not only to analyze existing tensioning methods, but also to select or develop tension devices which will improve the processing of yarn in any particular operation.

Post Tension

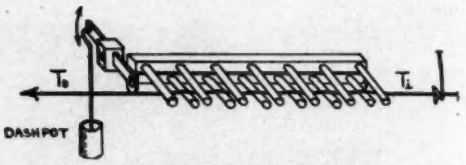
The simplest way to apply tension to a running strand of yarn is to snub the end around guides or posts with sufficient angularity to produce the tension required. In fact, all of the commercial tension devices incorporate this principle to some degree; in the classification of tension devices, the post tension (illustrated in Figure 5) was placed first. In this device one or more fixed posts are arranged so that the yarn comes into sufficient angular contact with the posts to establish the desired tension. The tension created by this arrangement may be calculated from the equation commonly referred to as the "belt tension equation," which in its simplest form is $T_o = T_i e^{fr}$, where T_o is the final or output tension, T_i is the tension on the strand before coming in contact



POST TENSION

$$T_o = T_i(e^{fr_1})(e^{fr_2})(e^{fr_3})(e^{fr_4})(e^{fr_5})(e^{fr_6})(e^{fr_7})$$
$$= T_i e^{f(r_1+r_2+r_3\cdots\cdots r_n)}$$

FIG. 5. *Diagram of post tension.*



GATE TENSION

$$T_o = T_i e^{f(r_1 + r_2 + r_3\cdots r_n)}$$
$$\text{WHERE } T_o = W(1-e^{-fr})/e^{-.5fr}(1-e^{-nfr})\sin\frac{r}{2}$$

FIG. 6. *Gate type of snubbing tension.*

with the first post, e is 2.718 +, r is the sum of the angles of contact of all the posts (expressed in radians), and f is the coefficient of friction of the yarn on the surface of the post. It will be observed from this equation that the output tension, T_o, will vary directly with the input tension; it will vary exponentially with both the coefficient of the friction, f, and the angle of contact, r. It is a simple matter to fix the angle of contact so that it will remain constant; if this is done, only two variables, T_i and f, are left. Then, if the input tension doubles, the output tension will also double. In withdrawing yarn from a bobbin or cone, the withdrawal tension is very low, so that the absolute value of T_i is normally very low. However, T_i may be subject to a relatively wide fluctuation due to the ballooning of the yarn or other causes. With this type of tension device, any small variations in withdrawal tension will be reflected in the final tension to a very great extent. The value of the coefficient of friction, f, is also subject to variation along the strand. Such variations may be due to nonuniformity of yarn finish, the speed of the running strand, twist, or even to the shape and surface of the fiber. Although these variations may be very small, their effect on the output tension is greatly magnified because of the exponential relationship. We refer to this type of tension as a "multiplying tension."

Finger Tension

There are many variations of the snubbing tension. Perhaps the most common variation is the one referred to as the gate, ladder, or finger tension; this type is illustrated in Figure 6. In this case there are a number of posts or fingers which create tension in the yarn in exactly the same manner as described for fixed posts, so that the tension may be calculated by the same basic equation; however, there is one major difference. The posts are so arranged that they may move back and forth, varying the angle of contact to compensate for variations in the input tension or the coefficient of friction of the yarn. At all times the tension on the yarn itself must react to support a fixed weight attached to the movable fingers. The amount of tension exerted on the yarn is largely determined by the amount of weight applied to the tension device. However, the compensation effected by this tension device bears a rather complex relationship to the output tension, as expressed by the second equation shown in Figure 6.* By way of example, let us suppose that the input tension increases. This would increase the tension all along the strand, thereby exerting greater force in opposition to weight W. In response to the increased force the fingers would move, reducing the angle of contact, r, which in turn would reduce the tension along the strand to restore the balance. The output tension in the meantime would have been altered in accordance with the equation to match the new value of r.

Stated in another way, we can say that within its operating range, increases in the input tension and coefficient of friction will cause the fingers to open, reducing their snubbing action so that the output tension tends to remain constant at a value determined by the tension weight. However, the compensation is not linear due to changes in the yarn path which alter the component of tension which supports the weight. The relationship between output tension and radius of contact, r, is shown graphically in Figure 7.

We might say, therefore, that the gate tension is capable of "compensating" for some of the variables which are multiplied in the post tension, but the compensation is only partially effective.

One of the difficulties of the gate tension is its low

* See Appendix for the derivation of this equation.

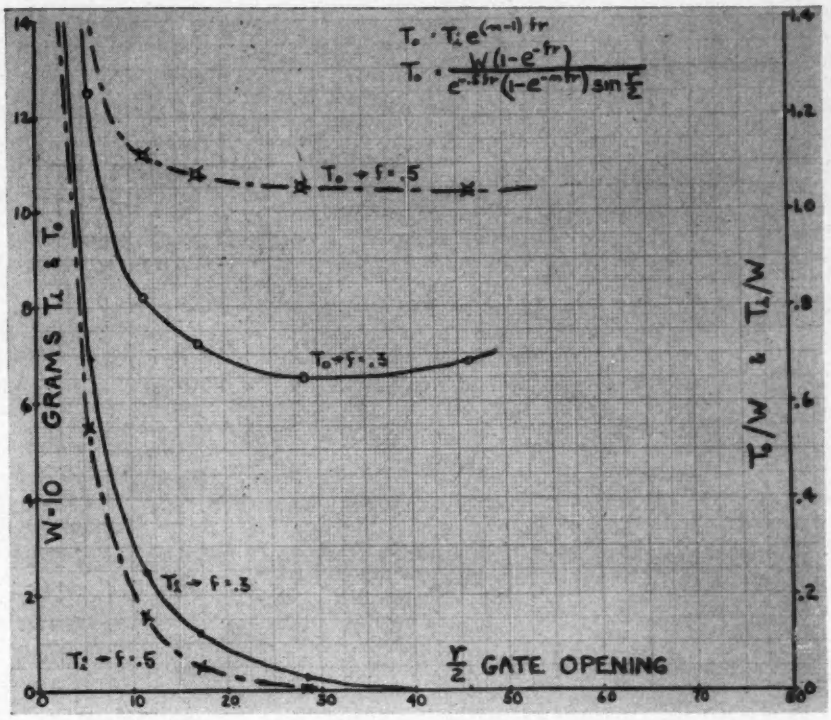

$T_o = T_i e^{(\alpha-\beta)fr}$
$T_o = \frac{W(1-e^{-fr})}{e^{-\beta fr}(1-e^{-\alpha fr})\sin\frac{r}{2}}$
T_o → f=.5
T_o → f=.3
T_i → f=.3
T_i → f=.5
W-10 GRAMS T_i & T_o
T_o/W & T_i/W
$\frac{r}{2}$ GATE OPENING
0 10 20 30 40 50 60 70 80
0 2 4 6 8 10 12 14
.2 .4 .6 .8 1.0 1.2 1.4

FIG. 7. *Relationship between output tension and radius of contact.*

natural frequency, which causes chatter. Therefore, in practice, it is necessary to use a dashpot to reduce the amount of chatter. If the damping due to the dashpot is too great, the compensating effect of the gate tension becomes negligible, and if too little damping action is present, the chatter of the gate tension may actually magnify tension fluctuations in the yarn.

Plate Tension

Let us consider next a plate or pinch tension, as illustrated in Figure 8. In this case there is no snubbing, and the tension is affected only by the force, W, exerted by the plate on the yarn and the coefficient of friction. We refer to this type of tension as an "additive tension" since it only adds to the initial input tension rather than multiplying it. The relationship between the coefficient of friction and the output tension is linear rather than exponential. Considering the small range within which the coefficient of friction normally varies within a given yarn, it is obvious that the output tension will be controlled within close limits by this device. This type of tension most nearly approaches the basic principle of additive tension devices.

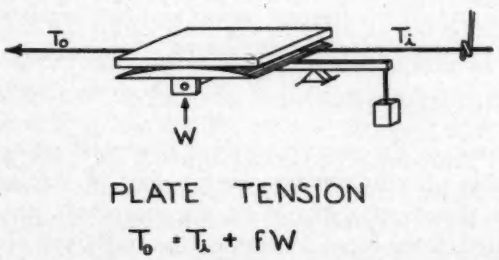


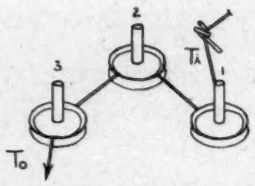
FIG. 8. *Plate or pinch tension.*

309° Disc Tension

In many of the tension devices in use we find both the multiplying and additive principles involved. This may be illustrated by a disc tension, as shown in Figure 9. In this particular setup are shown three discs mounted on posts so arranged that there is a total of 309° of snubbing around the posts. In calculating the tension derived from this apparatus, both the additive and the snubbing principles must be taken into account, as shown in the equation of Figure 9. Since the value of r in this equation is relatively large, this tension device would be expected to behave more like a post tension than a plate tension.

60° Disc Tension

Figure 10 illustrates a disc tension in which the yarn has only 60° of contact with the three posts. It is necessary to maintain a certain minimum angular contact to keep the yarn between the discs. Ex-



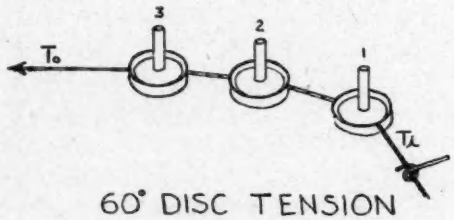
309° DISC TENSION

$$T_o = \{[T_i(e^{fr_1}) + fW_1]e^{fr_2} + fW_2\}e^{fr_3} + fW_3$$

$r_1 = 2.63$ $r_2 = 1.97$ $r_3 = .785$ RADIANS WRAP

$W_1 = W_2 = W_3 = 4.73$ GRAMS DISC WT.

FIG. 9. *309° Disc tension, using multiplying and additive principles.*



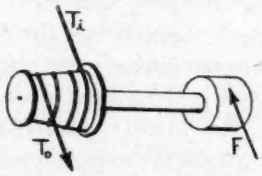
60° DISC TENSION

$$T_o = \{[T_i(e^{fr_1}) + fW_1]e^{fr_2} + fW_2\}e^{fr_3} + fW_3$$

$r_1 + r_2 + r_3 = 60°$ OR 1.047 RADIANS YARN WRAP

$W_3 = 1\frac{1}{2}W_2 = 3W_1 = 9.72$ GRAMS DISC WTS.

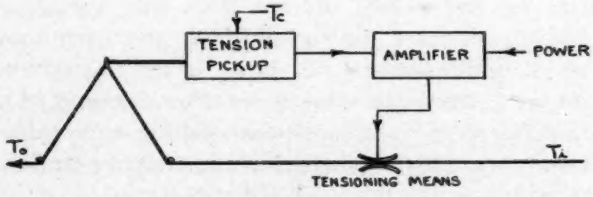
FIG. 10. *60° Disc tension.*



WHORL TENSION

$$T_o = T_i + F$$

FIG. 11. *Whorl tension.*



REGULATING TENSION

$$T_o \longrightarrow T_c$$

FIG. 12. *Diagram of apparatus which will maintain uniform tension.*

perience has shown that approximately 20° per post is about the practical minimum. This angularity also tends to promote the uniform rotation of the discs, thereby helping to keep them clean and minimizing wear. By holding the angularity to a minimum, it is possible to eliminate most of the snubbing action and thereby minimize the variation in T_o. It has also been found that the multiplying effect of the posts is minimized by the proper distribution of the weight on the discs. A light disc was used for post *1*, a slightly heavier disc for post *2*, and a still heavier disc for post *3*. The reason for this arrangement can be determined readily from the equation.

Whorl Tension

The two fundamental principles described above are the bases of the only two commonly used direct methods of controlling tension on the yarn. All tension devices which apply tension by frictional contact with the yarn may be defined in terms of the additive or multiplying principles discussed. On the other hand, there are certain tension devices which do not act directly on the yarn, but which are dependent on certain external forces which actually control the tension. One such device is the whorl tension, as illustrated in Figure 11. In this case the yarn is snubbed around the whorl with sufficient angular contact to prevent any slipping of the yarn with respect to the whorl. Therefore, the tension which is applied becomes a function of the retarding force applied to the whorl. This force may be derived from many sources, including frictional and magnetic effects. It is obvious that output tension derived from this device will be very little affected by the value of the input tension, which is always very small, or by the coefficient of friction of the yarn. It should be pointed out that the output tension will be only as uniform as the retarding force applied to the whorl, and it is difficult to hold this force constant. In this study a whorl tension was used in which the retarding force, F, was produced by a combination of magnetic and eddy-current braking and ball-bearing friction, in that order of significance.

Regulating Tension

None of the tension devices described above are capable of maintaining uniform tension throughout wide ranges of variation in the magnitude and frequency of the input tension or the coefficient of friction. It is possible, however, to design an apparatus

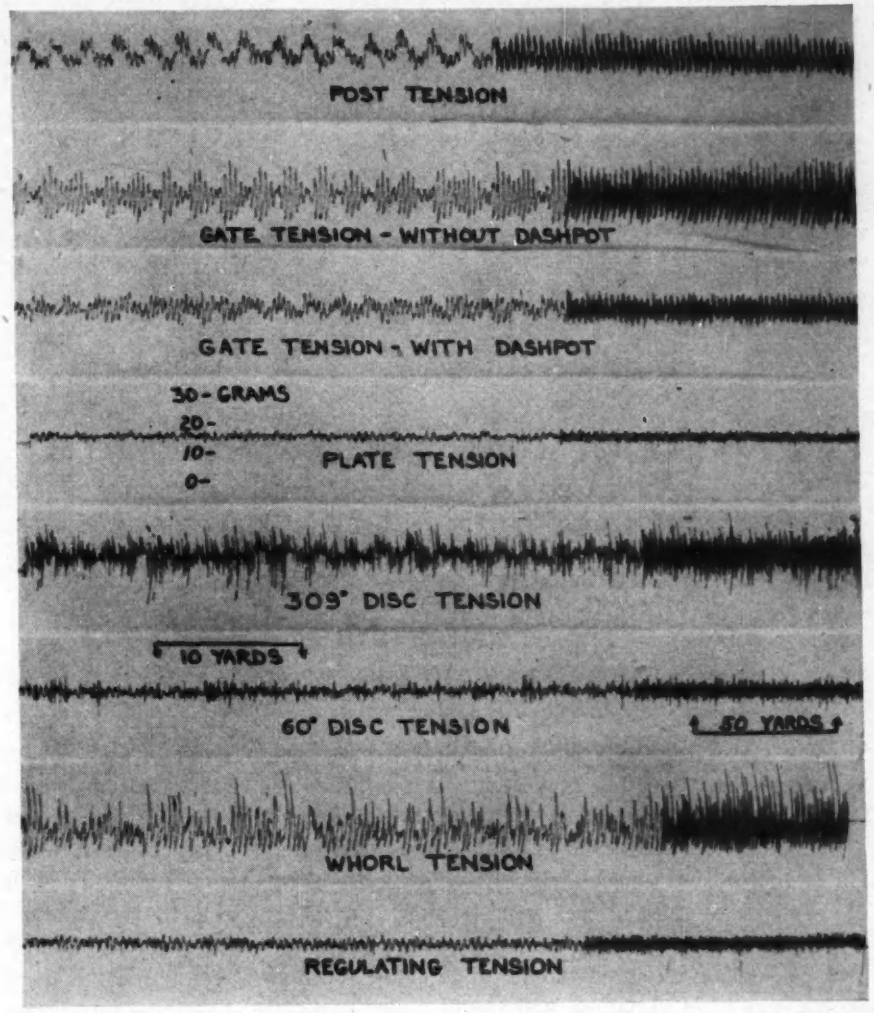


FIG. 13. *Short-term tension variations occurring from 0 to 100 cycles/sec.*

which is capable of accomplishing this. Figure 12 shows diagrammatically a laboratory control designed to provide a wide range of compensation for variations in yarn input tension, friction, yarn speed, twist, etc. In this apparatus, tension is applied by an electromagnetically actuated disc tension having a very fast response. A control loop in the yarn is used to measure the tension, and the output of the tension pickup is fed through an amplifier to an electromagnet. The electromagnet acts upon a steel disc which applies tension to the yarn in proportion to the current flowing in the control circuit. By properly designing the pickup and the auxiliary equipment, it is possible to obtain almost perfect tension compensation within all practical limits of operation. This device is somewhat complicated both in structure and in operation. It is included in this report only for its academic interest, since it is not readily adaptable for commercial use.

Experimental Data

High-Frequency Variations

Having classified tension devices into seven representative types, let us now consider the tension characteristics of each type under various conditions. Figure 13 shows the short-term tension variations occurring from 0 to 100 cycles/sec. For this test, 150-denier, 38-filament, 2-turn, dull yarn was used at the rate of 300 yds. per min. The chart was made while yarn was being withdrawn from the middle of the cone. The experiment was set up to give approximately the same average tension with each device—namely, about 15 g. The amount of the high-frequency tension variation, as shown in the graph,

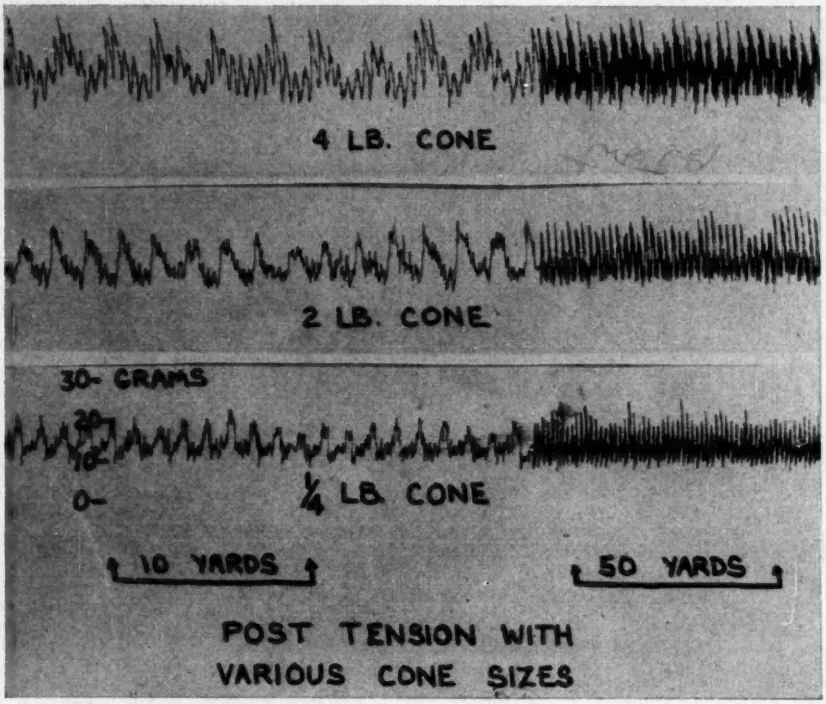


FIG. 14. *Tension curves.*

is more or less characteristic of each of the various devices tested. It will be noted that the magnitude of the variation corresponds closely to that which is predicted by the mathematical analysis discussed above. All of the tension devices which have a high degree of snubbing—namely, the post tension, the gate tension, and the 309° disc tension—show a high degree of tension nonuniformity. The plate tension shows very little variation, and the 60° disc tension is almost equal to the plate tension. The regulating tension is very similar to the plate tension. Obviously, the control mechanism was not fast enough in response to compensate completely for the variations at this high frequency. The whorl tension shows very high amplitude. We believe this to be caused by the yarn catching under itself on the whorl and creating a sluffing action which recurs with regularity every 3 or 4 revolutions. This condition might be overcome by changing the design of the whorl, although no work has been done on this.

By observing the oscillograph charts closely, it is possible to determine the source of some of the variations. The post tension, for example, shows two distinct frequencies. The lower frequency, which produces the variation of the greatest amplitude, corresponds to the traverse on the coning machine. The high-frequency variation, of slightly lower amplitude, which is superimposed on the traverse variation corresponds in frequency to the revolutions per second of the balloon around the cone. This will be shown more clearly later. In the gate tension the same fundamental frequencies are amplified somewhat by the chatter of the fingers. The addition of the dashpot tends to reduce the chatter to a very large extent. The disc tension with 309° wrap still shows the same frequencies, upon which has been superimposed a third higher frequency which is attributed to chatter in the discs, amplified by the posts.

Figure 14 shows tension curves which were made from cones of three different sizes. It will be readily observed that the frequency of the tension variations is inversely proportional to the cone size, further proving that the tension variation is largely caused by the action of the balloon and traverse motion. These curves were analyzed carefully, and an exact correlation was found in this respect. It would be well to point out that the total magnitude of the tension on the yarn as it enters the tension device is very small, although variable, in nature. This high-frequency variation is almost entirely attributable to input tension, T_i, and becomes objectionable only when it is greatly magnified by snubbing action.

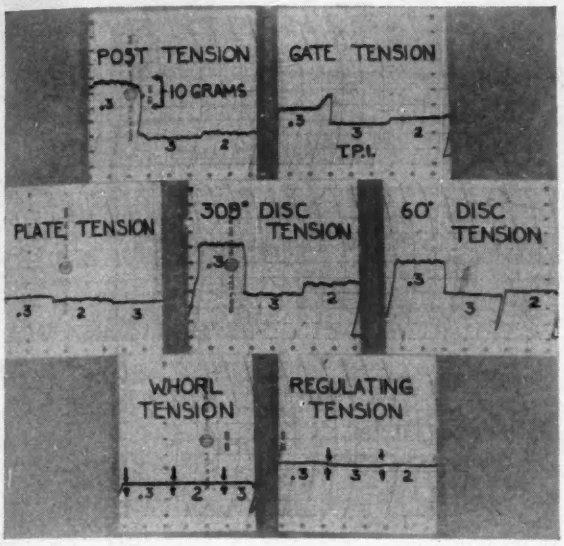


FIG. 15. *Effect of variations in twist on the final tension.*

Twist vs. *Tension*

It is a little more difficult to show directly the effect of variation in the coefficient of friction. One factor which affects the coefficient of friction and which can be controlled for test purposes is twist. We may assume that yarn in process must have considerable variation in twist along the strand. This may be caused by the snubbing action of guides or the tension device itself, which tends to push back the twist and permit it to move forward in surges. It is also quite possible that small variations in twist may exist from end to end or from yard to yard along a given end due to variables in the manufacturing process.

To show how such variations in twist might affect the final tension in warping measurements were made of the tension on cones which were wound from yarns having three different standard twists—namely, 0.3, 2.0, and 3.0 t.p.i. Several 1,000-yd. lengths of yarn of each twist were run on a cone. The yarn was withdrawn continuously at 300 yds./min., and the tension was recorded by means of the G.E. recorder. The results of this test are shown in Figure 15. Here again, the multiplying tensions tend to exaggerate the differences in proportion to the degree of snubbing involved. In this case it is the coefficient of friction which varies from sample to sample, and from the equation we would expect a large effect on the resultant tension due to the exponential relationship. The plate tension shows very little change in tension, indicating that the actual change in the coefficient of friction is relatively small. It is interesting to note that the gate tension registers a high level at the beginning of the 0.3 t.p.i. yarn and gradually drops off to a lower value. This is characteristic of the gate tension under the conditions of this test. It is probable that the twist is snubbed back by the action of the fingers, so that the first yarn passing through the tension gate has little or no twist. As the twist builds up behind the tension devices, it finally reaches the equilibrium value, as indicated by the flat part of the curve. Neither the whorl tension nor the regulating tension are affected to any great extent by the

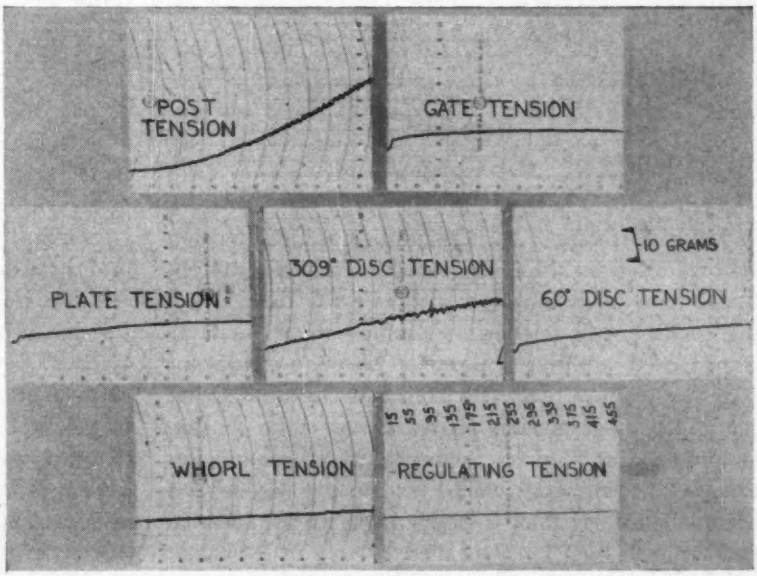


FIG. 16. *Effect of speed on tension.*

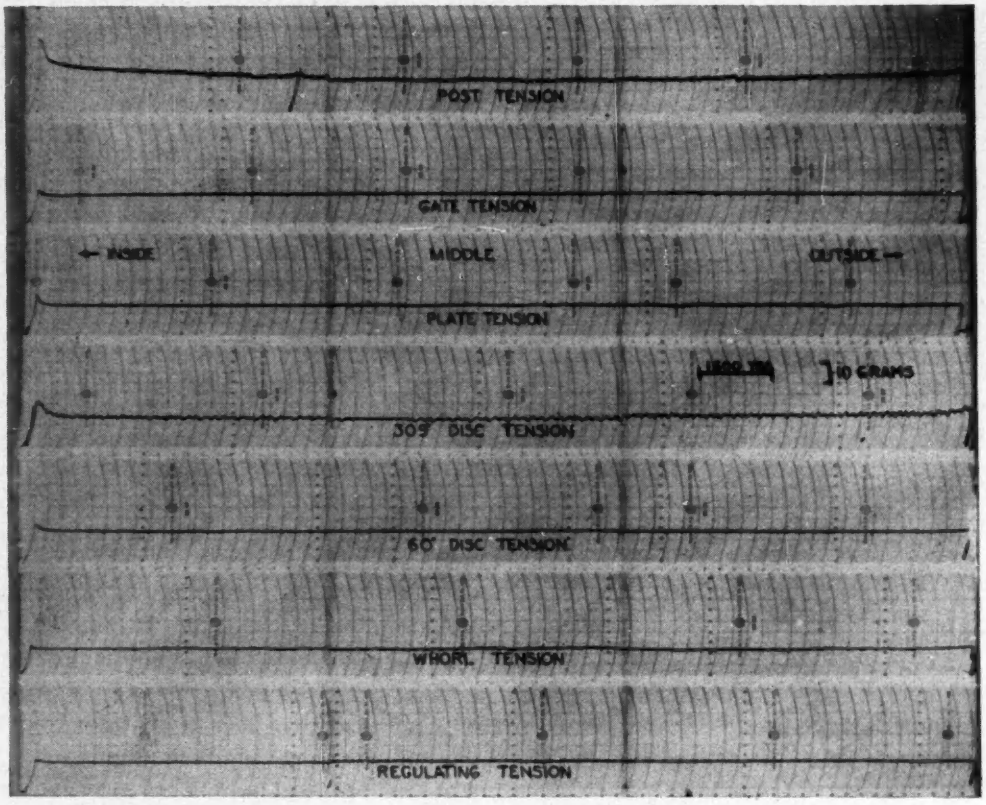


FIG. 17. *Performance of seven types of tension devices throughout full cones of yarn.*

variation of twist. This is logical since the coefficient of friction is not a determining factor in the tension obtained with either of these devices.

Tension vs. *Speed*

It is well known that the coefficient of friction of yarn varies with speed. This provides another opportunity to check the effect of the coefficient of friction. Figure 16 shows the effect of speed on tension. This test was run with 150-denier, 38-filament, 2-turn, dull yarn. The speed was varied from 0 to 455 yds./min. On the charts the speed was increased at a uniform rate of 40 yds./min./min.; the tension was recorded on the G.E. recorder. The results obtained here again show the large effect of the increasing coefficient of friction on multiplying tensions as compared to additive tensions. One very significant fact that may be observed from these results is that the simple post tension provides very little tension at low speeds. This is important in a beaming operation since the ends would tend to sag in the yarn sheet when the beamer is stopped. With the additive and compensating tensions there is very little change in tension throughout the normal range of warping speeds (150 to 500 yds./min.).

Tension vs. *Cone Size*

Finally, a series of tests more directly related to standard warping practice was conducted. In order to show the variations in tension which may be encountered in withdrawing yarn from cones, charts were prepared showing the performance of the seven types of tension devices throughout full cones of yarn. For these tests, 150-denier, 38-filament, 2-turn, dull acetate yarn was used. The withdrawal speed was 300 yds./min. The charts shown in Figure 17 are divided into three parts showing the tension on the first 6,900 yds., the middle 6,000 yds., and the last 6,000 yds. of yarn, respectively, from a 4-lb. cone containing a total of 120,000 yds. It has been found that most of the long-range tension variation within a cone occurs in the first few thousand yards and in the last few thousand yards. The tension between these sections remains almost constant. This is most clearly shown in the top curve made with a post tension. Although this type of tension cannot be recommended where

TABLE I

		Post	Gate*	Plate	309° Disc	60° Disc	Whorl	Regulating
Short-range variation								
300 yds./min., 2 t.p.i.	Low	11	11	13.7	10	11.5	9	12.5
Middle of cone	High	24	20	17.5	27	19	28	18
Tension *vs.* twist								
300 yds./min.	0.3 t.p.i.	266%	121%	109%	172%	159%	100%	101%
Middle of cone	2.0 t.p.i.	100%	100%	100%	100%	100%	100%	100%
	3.0 t.p.i.	86%	88%	91%	81%	91%	100%	97%
Tension *vs.* speed								
2.0 t.p.i.	15 yds./min.	20%	82%	74%	43%	64%	91%	96%
Middle of cone	215 yds./min.	100%	100%	100%	100%	100%	100%	100%
	455 yds./min.	315%	102%	111%	154%	118%	109%	104%
Tension *vs.* cone size								
2.0 t.p.i.	Outside	130%	104%	104%	142%	100%	108%	100%
300 yds./min.	Middle	100%	100%	100%	100%	100%	100%	100%
	Inside	226%	111%	125%	158%	116%	104%	102%

* With dashpot.

good tension control is desired, it is useful in studying the characteristic behavior of a given yarn due to the amplifying effect of the posts. It will be noted that the tension gradually drops off during the first 7,000 yds. to a constant level, which continues throughout the cone until only a few thousand yards are left. At that point the tension begins to rise gradually for about 5,000 yds., rising more abruptly to a peak as this yarn runs out. This pattern is again repeated by the other curves, showing the relative sensitivity of the various tension devices to changes in the coefficient of friction.

The cones which were used in this test were selected to show a significant variation. They do not necessarily represent normal behavior for acetate yarn. It is beyond the scope of the present study to interpret the causes for the variable frictional properties of the yarn within a cone. These tests were included to demonstrate that such variables do exist and that, even though they may be small, the use of an improper tension device may amplify them to troublesome proportions. The curve shown for the plate tension indicates that the long-range variation of the coefficient of friction within a cone is very small. Yet this small variation may cause serious difficulties when amplified with snubbing tension devices.

Summary

Table I summarizes the data which is shown in the various charts. This table shows the high-frequency tension variation expressed as a range in grams. The effects of twist, speed, and cone size are expressed as percentages, with the intermediate values taken as a base.

Table II shows the relative rank of the various tension devices for each of the tests made. In general, the compensating tensions give the best results. In the noncompensating types the rank is directly proportional to the degree of snubbing.

It has been shown that both high-frequency and long-range variations in tension may be encountered in warping yarn from cones. These variations may be almost completely eliminated by the use of properly designed compensating tension devices, but none of these devices are completely satisfactory due to certain practical considerations, such as cost, maintenance, and adaptability. Conventional tension devices which apply friction directly to the yarn without compensation will give completely satisfactory results provided that the angularity of the yarn path is held to a minimum. Such devices are generally simple in construction, low in cost, and trouble-free in operation. We believe that a multiple

TABLE II. RELATIVE RANK OF TENSION DEVICES*

	Post	Gate	Plate	309° Disc	60° Disc	Whorl	Regulating
Short-range variation	5	4	1	6	3	7	2
Twist	7	4	3	6	5	1	2
Speed	7	3	4	6	5	2	1
Cone size	7	3	5	6	4	2	1

* 1 = best; 7 = poorest.

disc tension with minimum snubbing, as described in this report, offers the most practical answer to the problem of tension control in warping. Although this discussion was limited to warping, the principles set forth are equally applicable to all other phases of textile processing where tension must be applied to yarn.

Appendix

Derivation of Gate Tension Equation

The equation relating the output tension to the compensation effected in gate tension is derived below. Figure 18 illustrates the forces influencing a gate tension.

The general force equations are as follows:

$$W = \sin\frac{\gamma}{2} T_i e^{.5f\gamma} + \sin\frac{\gamma}{2} T_i e^{1.5f\gamma} + \sin\frac{\gamma}{2} T_i e^{2.5f\gamma} \cdots + \sin\frac{\gamma}{2} T_i e^{(n-1.5)f\gamma} \quad (1)$$

$$W = \sin\frac{\gamma}{2} T_i (e^{.5f\gamma} + e^{1.5f\gamma} + e^{2.5f\gamma} + e^{(n-1.5)f\gamma}) \quad (2)$$

$$T_o = T_i e^{(n-1)f\gamma} \quad (3)$$

Substitute equation (3) in equation (2) and then solve for T_o and W:

$$W = \frac{\sin\frac{\gamma}{2} T_o (e^{.5f\gamma} + e^{1.5f\gamma} + e^{2.5f\gamma} \cdots + e^{(n-1.5f\gamma)})}{e^{(n-1)f\gamma}} \quad (4)$$

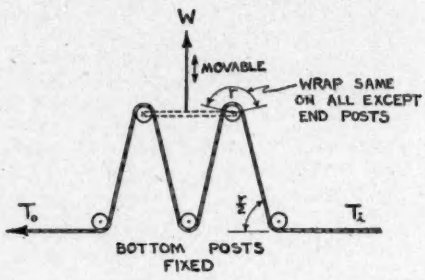


FIG. 18. *Forces influencing a gate tension.*

$$W = \sin\frac{\gamma}{2} T_o (e^{(1.5-n)f\gamma} \cdots + e^{-1.5f\gamma} + e^{-.5f\gamma}). \quad (5)$$

By using the geometric series summation form,

$$\Sigma[a + a\gamma + a\gamma^2 + a\gamma^3 + a\gamma^4 \cdots + a\gamma^{(n-1)} = \frac{a(1-\gamma^n)}{1-\gamma}, \quad (6)$$

and substituting $a = e^{-.5f\gamma}$ and $\gamma = e^{f\gamma}$, to get

$$\Sigma(e^{(1.5-n)f\gamma} \cdots + e^{-1.5f\gamma} + e^{-.5f\gamma}) = \frac{e^{-.5f\gamma}(1-e^{-nf\gamma})}{1-e^{-f\gamma}}, \quad (7)$$

we obtain the equation for a gate tension:

$$T_o = \frac{W(1-e^{-f\gamma})}{e^{-.5f\gamma}(1-e^{-nf\gamma})\sin\frac{\gamma}{2}}. \quad (8)$$

(Manuscript received April 24, 1952.)

Book Reviews

Radioisotopes; Industrial Applications. G. H. Guest. New York, Pitman Publishing Corp., 1951. 185 + xv pages. Price, $4.50.

(Reviewed by H. M. Isikow, U. S. Testing Company, Inc., Hoboken, N. J.)

After devoting its opening chapters to a very brief and elementary review of the nature of the atom and of the nuclear transformations by which radioisotopes are prepared and by which they decay, this volume settles down to detailing an interesting variety of both accomplished and suggested applications of radioisotopes in industry.

There is a dual format in which these applications are grouped according to industry and according to whether the radioisotopes are employed as tracers or as important primary sources of radiation. As a result of this duality, there are a few cases in which subject matter and references are duplicated. Among the industries considered, metallurgy claims the lion's share of space, with the ceramics and glass, petroleum, rubber, chemical (textiles, paper, paint, inks, analysis, research), and miscellaneous fields sharing much of the remainder. In these chapters, radioisotopes fall into the tracer category. A number of the above industries are reintroduced in subsequent chapters, where radioisotopes are discussed as sources of radiation, in employments such as radiography, static-charge elimination, and thickness and liquid-level gaging.

In the textile field, the use of sodium-24 oleate to check the uniformity of distribution of lubricants on fibers is described, along with suggestions for employing the tracer technique in studies on the mechanism of dyeing, on the desulfurization of viscose rayon, and on the automatic process control of dyebath concentration.

The design of laboratories for working with low-to-intermediate levels of radioactivity and the precautions to be observed in handling radioisotopes are dealt with in the concluding sections.

References are appended to each of the chapters, while the appendixes provide lists of reference books and pamphlets as well as tables describing available radioisotopes, their half-lives, and their characteristic radiations. The text is notably free from typographical errors; "deutroms" on page 79 should read "neutrons."

This volume is recommended to those who wish to learn something of the myriad potentialities for the application of radioisotopes in solving some of the knottier problems of industry. Those who are conversant with the field and who keep abreast of the literature will find comparatively little to occupy them here.

Phase Microscopy—Principles and Applications. Alva H. Bennett, Helen Jupnik, Harold Osterberg, and Oscar W. Richards. New York, John Wiley & Sons, Inc., and London, Chapman and Hall, Ltd., 1951. 320 pages. Price, $7.50.

(Reviewed by F. F. Morehead, American Viscose Corporation, Marcus Hook, Pa.)

The most interesting and promising developments in the field of instrumentation in light microscopy is that of "phase contrast" or "phase microscopy," the latter term being used preferentially by writers in this country.

This book very completely covers this new field in both its theoretical and practical aspects. The work is of interest to both the tyro and the experienced microscopist because it contains not only simple directions and explanations, but also a complete theoretical and mathematical treatment of the subject, which is a refreshing contrast to the many manuals of microscopy that are merely compendiums of directions and "cookbook" recipes.

The four authors of the book have contributed ably in their special fields: Mr. Bennett, the introduction and general editorship; Dr. Jupnik, the instrumentation; Dr. Osterberg, the theory and mathematics; and Dr. Richards, the chapters on using the phase microscope and its applications to biology, medicine, and industry.

The section on Comparison of "Phase Microscopy" with Other Methods is of special interest. The opening paragraph and part of the succeeding text are as follows:

"When absorption is adequate and relatively selective, the specimen may be examined with bright-

field, ultraviolet or infrared microscopes, depending on the region of the spectrum absorbed. When absorption is too weak, from inadequate staining or slight pigmentation, the phase microscope may add enough contrast to permit examination, and it may also reveal fine details that would be overlooked with bright-field methods on specimens of fairly low contrast.

"Transparent specimen with internal detail due to differences in optical path may be examined with optical staining, dark field, interference, polarizing and phase microscopy. When the optical path differences are small, the phase microscope is preferable. With larger differences in optical path the dark field and ultramicroscope are preferable. . . ."

The final paragraph contains the warning that phase microscopy will not supplant, but rather supplement, conventional methods:

"Rarely is a specimen found for which one, and only one, microscope method is entirely adequate. Usually the image formed is a result of the different properties of the specimen acting together on the radiant energy used for probing its content, and each method of microscopy will reveal additional information. The ideal microscope should be fitted for all methods. Since this is not practicable at the present time, the appropriate methods must be chosen with respect to the specimen and the objective of the investigation."

In the chapter on the industrial applications of phase microscopy, the following subheadings are of interest to the textile field both for practical use and for research: Fat, Grease, Oil and Soap; Paint and Pigments; Paper; and Textiles.

One unique feature of phase microscopy is its ability to define an edge in tones of gray rather than as a line. This is of considerable use in fiber microscopy in locating exactly textile acids such as sizes, finishes, or resin treatments, especially if the material in question can be stained. Another time-saving supplementary use is in connection with electron microscopy—the pre-examination of specimens by the phase microscope before using the electron microscope.

A very valuable part of the book is its extensive bibliography, the extent of which indicates the interest in the new microscopical tool, phase microscopy.

The Theory and Practice of Wool Dyeing. C. L. Bird. Second Edition. Bradford, England, Society of Dyers and Colourists, 1951. 231 + xvi pages. Price, 15s., postage prepaid.

(Reviewed by G. L. Royer and H. E. Millson, American Cyanamid Co., Calco Chemical Division, Bound Brook, N. J.)

This book is a revised and extended version of the first edition published in 1947. The illustrations have been increased from 58 to 77, and the total pages of text from 207 to 231.

The primary purpose of the book is to help students prepare for examinations in wool dyeing; therefore, the author condensed much of the information without sacrificing the essential facts. The first chapter orients the reader by showing the relation of dyeing to other textile processes, since the latter often influence the results obtained in dyeing. Wet treatments such as scouring, milling, crabbing, potting, bleaching, carbonizing, and chlorination are described in detail. Chapters on the chemistry and application of acid, milling, chrome, and premetallized dyes to wool are especially informative. The union dyeing of wool blended with fibers such as viscose, acetate, silk, and nylon is discussed in detail, and is timely because of the current trend toward the greater use of wool-synthetic fiber blends.

The book contains valuable information on the leveling of dyes, stripping, water, and auxiliary products, a knowledge of which is necessary for the successful application of dyes to wool and other textile fibers.

The section on machinery has been extended to include a description of many new and conventional dyeing machines. It is profusely illustrated with photographs, schematic drawings, diagrams, and cross-sections of the different types of equipment now in use for the dyeing of wool in all of its varied forms—*i.e.*, raw stock, slubbing, yarns, and pieces.

The chapter on the theory of wool dyeing is well written, and includes many references for further study. This is supplemented by an appendix on the mathematics of the Gilbert and Rideal equation for the expression of the dyeing of wool and by an appendix on acidity and alkalinity as they affect dye solutions and chemicals.

The book is recommended as a textbook and for reference purposes to both textile chemists and colorists.

Handbook of Dangerous Materials. N. Irving Sax, assisted by M. J. O'Herin and W. W. Schultz. New York, Reinhold Publishing Corp., 1951. 848 + viii pages. Price, $15.00.

(Reviewed by R. O. Steele, Textile Research Institute, Princeton, N. J.)

In his preface, Mr. Sax says, ". . . this book is directed not only to the industrial physician and trained safety inspector in industry, but to foremen and plant managers, who have neither the time nor the inclination to make a deep study of possible toxic hazards that might occur in their shops. It is also intended for research and development laboratories and pilot plant workers who use a wide variety of materials and who often need reliable safety data concerning them." He has indeed accumulated and classified a large amount of information on the dangerous properties of materials which are the concern of the classes of people mentioned above. Most of this information is in Section I, comprising almost half of the book, which is an alphabetic listing of materials, together with information on their hazardous properties, their handling and storage, and the applicable shipping regulations.

Section II (56 pages) is concerned with the safe handling of explosives. Much of the material in this section apparently was reprinted from Bureau of Mines and Army publications. In Section III (64 pages) M. J. O'Herin has described the symptoms and treatment of the known fungus diseases, and listed the uses and hazardous properties of a number of fungicides, including proprietary products. The fourth section, by Warner W. Schultz, is concerned with radiation and its hazards. The chief emphasis is on the nature and measurement of radioactivity, which is reasonable in view of the intended readers of the book. However, it is questionable whether a complete chart of the known nuclides will be of sufficient use to justify its occupying 24 of the 69 pages in this section.

Section V (223 pages) consists of the complete text of the shipping regulations of the Interstate Commerce Commission, as issued by the Bureau of Explosives. This section contributes to making the book large and relatively expensive, but references in Section I to the regulations for the various materials described there make this section convenient.

The book has a satisfactory index and physical makeup, and should be a useful reference for the various groups of workers for which it is intended.

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A series of cationic nitrogen compounds for softening and finishing textiles.

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Well over a million pairs of DYNEL socks have now been sold. Their cashmere-like hand, extraordinary wear-life, comfort, good looks and easy care are inherent sales advantages that bring increasing repeat business.

In manufacture, they have proved easy to knit, dye and finish.

KNITTING DYNEL HOSE

Standard equipment of many types is used in knitting DYNEL. All that is normally required is customary adjustment of tensions before knitting. The knitter has full flexibility in choosing construction from yarns ranging in size from 4/1 to 50/1, cotton count. Yarns as received are properly lubricated.

For optimum results, the Knitting, Dyeing and Finishing Departments should work closely together to determine proper construction. As received, DYNEL yarns normally have from 1.5% to 5.0% boiling water shrinkage, depending on the yarn size, twist and spinning system used by the yarn supplier. This shrinkage, plus shrinkage in dyeing, must be allowed for in sock construction—usually from ½ to 1 inch. A minimum of from 2 to 4 courses of cotton or elastic in the top of the welt of all socks will aid in boarding.

DYEING

At present, DYNEL elastic top socks and half hose are being successfully knitted, piece dyed and finished from natural yarns; Argyles and slipper socks from package dyed yarns.

Excellent results are obtained by dyeing the socks loose in paddle or rotary type machines, but some mills are also using nets with great success.

Acetate dyes are currently used almost exclusively for piece dyeing. These colors level exceptionally well, are washfast and lightfast, are easy to apply. Procedures are normal, except to maintain bath temperatures somewhat higher than usual and to cool the bath slowly to prevent wrinkles or creases. Light shades are simply rinsed, darker shades are scoured. Key to obtaining a full lofty hand is assuring that the socks float freely during all wet processing steps.

FINISHING

After dyeing and proper cleaning, the goods are finished with 1% Amide PES, made more permanent with glyoxal. This gives a desirable soft hand and minimizes the tendency to develop static electricity.

The goods should be extracted in a centrifuge for as long a period as possible. There is no danger of wrinkles setting in DYNEL socks during extraction. Before boarding, however, they should be thoroughly dried by simple air drying or by tumbling at 170°F. or lower.

BOARDING

Steam pressure should not exceed 5 to 7 pounds per square inch, when boarding is done on internally steam-heated forms. On continuous machines, operating temperatures should range between 215°F. for lightweight socks and 235°F. for the heavier weights. For best results with continuous machines, socks should be cooled as they leave the oven to prevent distortion by automatic stripping machines. A simple cooling method is to direct cool air from the mill's air conditioning system on the forms.

Identification transfers designed for DYNEL are readily applied to the socks. Temperatures used must be established by the mill.

DYNEL in socks is just one example of the ease of processing and the exciting sales possibilities of this exciting new fiber. For full information on knitting specifications, dyestuffs and dyeing procedures and finishing recommendations, write: Textile Fibers Department, Carbide and Carbon Chemicals Company, A Division of Union Carbide and Carbon Corporation, 30 East 42nd Street, New York 17, New York.

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Cashmere-like hand	Extraordinary wear
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